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ORGANIC REAGENTS USED IN QUANTITATIVE INORGANIC ANALYSIS

ORGANIC REAGENTS

USED IN

QUANTITATIVE INORGANIC ANALYSIS

BY

WILHELM PRODINGER, PH.D.

TRANSLATED AND AMENDED FROM THE SECOND GERMAN EDITION BY

STEWART HOLMES

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WITH A FOREWORD BY

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FOREWORD

The book of Prodinger demonstrates clearly the importance, usefulness and necessity of organic reagents for the modern analytical chemist. This statement may seem very natural for the chemists and students of today, but it was foreign 30 years ago at the time I became interested in the analytical application of nitrosohydroxylamine compounds.

In 1909, the great work of Alfred Werner was indeed appreciated only by a select group of scientists, despite the fact that since 1893 Werner, with numerous coworkers, had already laid a concrete basis for his theory. If we compare Werner's marvelous experimental work with the experimental achievements of Faraday and look for a mathematical background, then we find that Werner stood alone while Faraday had his Maxwell.

Werner's theory of complex compounds will stand for all time because of the overwhelming experimental work, not only by the Werner school alone, but also by numerous other research workers. Again and again it has been proven that Werner ideas were right. The analytical chemist who uses organic reagents will profit much and will become more deeply interested in the fascinating chapters of Werner complexes when he reads Prodinger's book carefully. It is not so much the question of finding more and more organic compounds applicable in analytical chemistry but to find new facts which have a bearing on the theory of specific affinity. Today we cannot yet predict to which metal a certain organic atomic grouping will react specifically, or selectively, and our work is left almost entirely to chance. I believe that the systematic study in the field of organic metal complex compounds and their application in analytical chemistry will lead, in the near future, to surprising results.

O. Baudisch.

TRANSLATOR'S PREFACE

Because organic reagents have proven of such utility, numerous publications have appeared in the technical literature concerning their use. This monograph of Prodinger's is a fine attempt to correlate this widely scattered material into a concise, usable form. The book appealed to me as worthy of publication because there is no equivalent in the English language and because it is filled with valuable procedures and ideas that offer a great deal of opportunity for development both by the practical analyst and the research chemist. It is hoped that the availability of this book in English will stimulate and nurture this new movement in analytical chemistry.

The book is a fairly literal translation of the German. It has been revised in a few places and because of its wide use and importance, two sections pointing out a few of the applications of 8-hydroxyquinoline or "Oxine" and α-nitrosonaphthylhydroxylamine Ammonium or "Neocupferron" have been added.

To my chief and teacher, Dr. Oskar Baudisch, I express my sincerest thanks. His advice and encouragement has been invaluable. I would also like to thank Solomon Penner, Dorothy Folts and Beatrice Weidman for their assistance in preparing the manuscript, etc.

STEWART HOLMES.

Saratoga Springs, N. Y.
July, 1940

FROM THE PREFACE TO THE SECOND GERMAN EDITION

When not quite two years ago the first edition of this volume appeared, one would not have supposed that a new edition would be necessary in so short a time.

This gratifying fact as well as the many favorable criticisms in the technical literature have shown me that I succeeded in filling a definite need in the analytical literature.

There was no apparent reason, therefore, to alter the arrangement of the material in the first edition whose purpose was neither a pure "textbook" but still less, a "cookbook."

It is for this reason that I could not write the composition desired by the critics. This book would have contained the determinations possible with the reagents discussed and a classification of their practical applicability. In the text of the first edition, I had already interwoven references as to the advantages and disadvantages of the individual methods wherever this seemed desirable. In this new edition, I have attempted to increase the applications from the literature of the technical analysis.

A strict classification or discussion of the individual methods would necessitate a systematic checkup that would be a long wearisome job for one individual.

Here I would like to ask a favor from my colleagues; that they inform me of their observations and experiences with these methods and that they help by sending pertinent reprints.

The following reagents were newly added: dimethylglyoxime, phenyl arsenic acid and thiourea. At the end of the book, some less frequently used precipitating agents have been added whose use might be recommended in some cases.

However, in the case of dimethylglyoxime the reactions described in every analytical chemistry book which—as one may well say—belong today to the classic ones were not included. For the same reason, the determination of sulfuric acid with benzidine according to Raschig has not been taken up since, for instance, this method was described in detail in Treadwell's well known book.

It is a pleasant duty to thank heartily Prof. Wilhelm Böttger for his valuable advice and pointers in preparing this second edition.

I do not like to close without thinking once more of my learned teacher, Prof. A. Franke, Wien. That which I have learned in his school laid a foundation for the composing of this book. Some time it may possibly become an important contribution to the chemical literature.

WILHELM PRODINGER.

Frankfort, a. M., S. 10
The end of January 1939

PREFACE TO THE FIRST GERMAN EDITION

Organic reagents are being used in ever increasing numbers for carrying out quantitative determinations. In this book, an attempt has been made to survey the most important organic precipitants not only with the sincere purpose of collecting and interpreting this interesting chapter of analytical chemistry in one volume but also with the hope that the practical analyst will find some useful applications and the possibility of further development of his work.

The general desire for rationalization of analytical procedures raises the question of whether or not the use of relatively expensive reagents is to be recommended.

There can be no real doubt as to the value of organic reagents since they give more exact results and in a far shorter time than other reagents used so far. If one considers further that the high sensitivity, i.e. the low limit of identification, and the correspondingly far-reaching precipitation of the cations permits, in many cases, the use of micro analytical procedures needing only a few milligrams, then the high initial cost has no real significance.

Thus the organic reagents are interesting not only from a theoretical standpoint but their significance in analytical chemistry is well on a par with their theoretical considerations.

In the execution of the work outlined above, I have been aided by advice and ideas of the editor of this collection, Prof. Wilhelm Böttger.* I take this opportunity to express my heartiest thanks.

WILHELM PRODINGER.

Mainz, in April 1937

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* The German edition is a part of the series Chemische Analyse.

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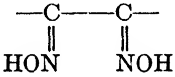
GENERAL PART

A. Introduction

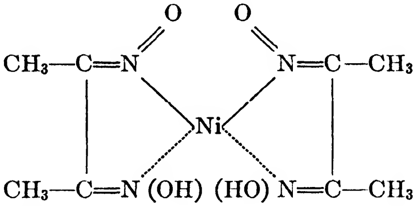
Because analysts have long desired to use methods of determination which possess high sensitivity, vast specificity and rapidity of operation, their interest has been directed to the combination of metals with organic reagents. The study of molecular organic compounds (1) provided the foundation which today makes possible a systematic search for new reagents. This search soon brought out that the various metallic ions, in general, react only with organic molecules of special structure; that is, certain atom groupings are specific for certain metals. Not only does dimethylglyoxime form the well known, characteristic precipitate with nickel ions, but this property is common to many antidioximes of the 1,2 diketone type. Thus the atom grouping,



$$\begin{array}{cc} -\text{C}-\!\!\!-\!\!\!- & \text{C}- \\ \| & \| \\ \text{HON} & \text{NOH} \end{array}$$

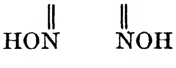
may be considered specific for nickel.

Pfeiffer (2) has shown that nickel dimethylglyoxime,



is an inner complex salt.

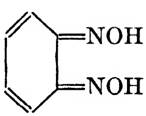
The capability of the group,



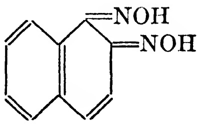
$$\begin{array}{cc} -\text{C}-\!\!\!-\!\!\!- & \text{C}- \\ \| & \| \\ \text{HON} & \text{NOH} \end{array}$$

, to form

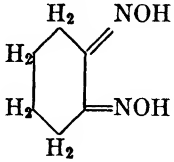
innercomplex salts is essentially influenced by the character of the attached molecule. In dioximes of the type,



or



the specific activity of the above mentioned group has disappeared. The napthaquinonedioxime forms a brown-yellow precipitate with nearly all metals. These precipitates may be regarded as merely the normal salts of a dibasic acid. The specificity returns, however, if the double bonding in the aromatic rings is removed through hydrogenation. Cyclohexadienedioxime,



for instance, forms a nickel salt which is not externally distinguishable from nickel dimethylglyoxime (3). From this discussion, it is at once apparent that the specific effect of the two oxime groups is destroyed by aromatic ring linkage.

Similar to dimethylglyoxime, many organic reagents also react to form complex salts. Therefore a short survey elucidating these types of compounds follows.

As is well known, the compounds of inorganic chemistry are divided into a first, second and a higher order. First order compounds can be recognized by the fact that their atomic affinity (as shown by the valence) is satisfied—as provided by the original valence theory. Often, however, compounds of the first order react with each other to form compounds of the second or higher order; $SiF_4 + 2HF = H_2SiF_6$. It is impossible to explain the formation of such compounds with the classic valence theory. Alfred Werner (4) gave an explanation—today generally accepted—of this phenomena in his theory of covalence. According to his theory, an atom possesses, besides the principal affinity as expressed in the valence, an additional amount of this affinity. This excess is the *covalence.* The number of atoms or atom groups which may be linked to a metal atom through principal—or covalence determine the coordination number of the nuclear metal atom. This coordination number is not a constant, but is different from case to case. However the variability is not so pronounced as the valence of the atom. The coordination numbers most commonly appearing are 6, 4, 3 and 2. Atoms (in the inner sphere) bound through covalence or coordination are, in the presence of principal valent forms, not ionically united.

The complex compounds are divided into three main types: *addition* compounds, *penetration* compounds and *inner complex* compounds. Addition and penetration compounds are so formed that a central atom coordinates several atoms or polar molecules. The number of these atoms or molecules constitutes the coordination number.

The addition compounds are characterized by the fact that the direct union between the cation and the anion is not changed in the solid or dissolved state, for example, the addition compound of pyridine and chromic chloride, $CrCl_3 \cdot 3Py$ (where Py = pyridine, C_5H_5N).

Penetration compounds are formed by the union of so-called neutral substances such as water, ammonia, ethylenediamine and others to an ion. The original complex ion forms a new, dissociable molecule by satisfying the principal valences with another ion, binding it in the secondary ionic sphere. For instance, $[Cu(NH_3)_4]SO_4 \rightleftarrows [Cu(NH_3)_4]^{\cdot\cdot} + SO_4''$.

If a metallic or non-metallic atom is coordinated to a different atom of the same molecule, then we speak of an inner complex compound. In these compounds, the metal forms a heterocyclic ring in satisfying the principal and covalence. The same rules hold for these rings as in those rings united only by principal valences. The inner complex salts correspond to the promotion of the Baeyer strain theory: the same arrangement of 5 and 6 membered rings is especially preferred (or especially stable) (5) (1).

Such inner complex salts have an abnormal analytical action such as the absence of normal precipitation reactions of the corresponding ions and a very small solubility of certain salts in water. On the other hand they often exhibit excellent solubility in organic solvents, e.g., ether, chloroform, etc. A further criterion is the characteristic type of light absorption as indicated by the abnormal colors of inner complex salts. This abnormality is a result of the covalent saturation between the organic residual affinity and the metal atom.

The inner complex salts are of value for analytical purposes because of their minute solubility in water. As a result they possess a higher sensitivity and also the precipitation reaction is much more complete than that of other types of reagents. Thus these methods of determination are excellently suited for the detection and estimation of the smallest quantities. The precipitate is, in many cases, already in an ideal weighing form; the ions to be determined are imbedded in a heavy complex of extremely favorable conversion factor and often attain constant weight rapidly as well as being very stable in air. Because of these properties, those methods of microgravimetric analysis* which employ inner complex salts as the precipitating and weighing medium can be utilized most advantageously.

In those cases where direct weighing of the complex is impossible, its color can often be successfully adapted to colorimetric determination.

As was already pointed out, the organic precipitants are distinguished by their specificity. Just lately, however, certain discoveries have led to a limitation of this conception. They showed namely, that if a reagent was not in itself specific, it may be changed by following certain conditions—such as an exact pH concentration—to a specific one. These procedures are explained in more detail in the special part of the discussion relegated to individual reagents.

The "Union Internationale de Chemie" has set up a commission for new reagents which differentiates between specific and selective reagents.

Reagents which react with but one substance under determined experimental conditions are called *specific.*

Reagents which only react with a very few substances under the experimental conditions are termed *selective.*

Thus depending on whether a reaction, or a reagent is more or less selective, the reaction, or the reagent is designated as specific or non-specific.

A further possible use of organic reagents is offered by penetration compounds which form organic bases with heavy metal ions (ethylenediamine, propylenediamine, benzidine, etc.). These complexes are also very stable and often separations are made possible which can be carried out only with difficulty or incompleteness by the established methods.

The adsorption of metallic compounds by means of organic adsorbers, for example, the tannic acid sol, has also demonstrated itself to be a valuable addition to analytical procedures.

---

* Consult the work of F. Hecht and co-workers.

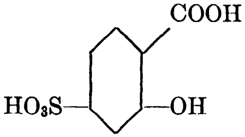
"The analysis of very small amounts of Morogon-Uranite." *Mikrochemie* (N.F.) **10,** 45 (1931).

"Methods of micro analysis with special reference to the analysis of Gordonia-Uranite." *Am. J. Sc.* **27,** 321 (1934).

"Complete micro analysis of Ceylon-Thoranite." *Mikrochemie* (N.F.) **12,** 193 (1932); see also *Mikrochemie* (N.F.) **12,** 281 (1932/1933).

"The importance of micro analysis of radioactive minerals in measuring geological time." *Z. anal. Chem.,* **106,** 82 (1936).

Another group of reagents form soluble complexes which are characterized by their action with other reagents. Sulfosalicylic acid,



which possesses three different strongly acidic hydroxyl groups is a good example. By adding the salt of the corresponding acids, it becomes possible to make either the sulfonic acid and the carboxyl group or the sulfonic acid group alone form salts. If, for instance, ammonium carbonate is added to the sulfosalicylic acid solution, then the carboxyl and the sulfonic acid group become masked and the acidity is due only to the effect of the acid phenol group:

$$C_6H_3(OH)(COOH)(SO_3H) + (NH_4)_2CO_3 \longrightarrow$$
$$C_6H_3(OH)(COONH_4)(SO_3NH_4) + CO_2 + H_2O$$

On the other hand ammonium oxalate masks only the sulfonic acid group. Through liberation of hydrogen ions from the free acid groups always present and through concentration of them or of the anion, a certain pH in the solution is reached, a property which makes possible numerous applications.

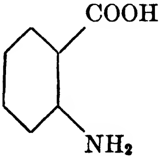
Before presenting the individual methods, the most important reagents are briefly compiled to make possible coherent discussion of the general chemical conduct. The reagents are classified as follows: The reagents which form normal salts, form complex salts and finally those which form metallic adsorption compounds are each grouped into their particular classification.

It is naturally not intended to discuss procedures for individual compounds in this part; to the contrary, only that which is pertinent to the analyst will be discussed.

B. Reagents Which Form Normal Salts

1. *Anthranilic Acid,*

$C_7H_7O_2N$,



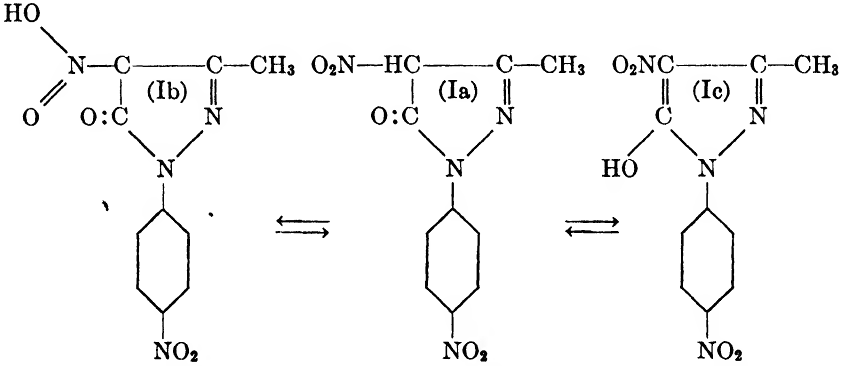
M.W. 137.06

The acid can be rather easily purified by recrystallizing out of alcohol, dilute alcohol and finally out of water containing active carbon. (Since the reagent must be purified to reagent grade by recrystallization, it is best to start out with the commercially pure material because the cost is considerably less.) The melting point of the pure acid is about 145°C. The alkali salts, which are easily soluble in water, show a light yellowish color in concentrated solutions and a white blue fluorescence in dilute.

Zinc, cobalt (II), nickel, cadmium, copper, lead and mercury (II) salts crystallize easily, are insoluble in water and alcohol and are not hygroscopic (6). They all filter easily and are extremely stable if kept between 105 and 110°C. It is recommended to use the reagent for detecting relatively small quantities.

2. *Picrolonic Acid,* $C_{10}H_8O_5N$, M.W. 264.1

The acid, 1-p-nitro-phenyl-3-methyl-4-nitro-pyrazolone-5, is a derivative of pyrazolone having the following formula (Ia):



Both of the desmotropic formulas 1b and 1c are possible for the acid, they both bring out the acidic character. For salts the formula 1b is more likely since then the picrolonic acid forms salts as the pseudo acid derived from the *aci*-form. A salt derived according to the tautomeric formula 1c is not likely to correspond in its properties to calcium picrolonate. It is necessary in this case to suppose that the p-nitrophenyl group makes use of covalence. Then the salt has the characteristics of an innercomplex compound. On the other hand the color and also the solubility of the salt are against this theory.

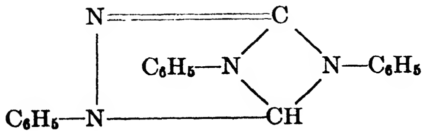
The reagent prepared by the firms E. Merck, or F. Kahlbaum, begins charring at approximately 111°C. in the melting point determination and when heated somewhat higher, it is destroyed. Chemically pure picrolonic acid, which can be prepared by recrystallizing the trade product from 33% acetic acid and then from a little alcohol, melts at 116.5°C.

Depending on the methods by which the solution of picrolonic acid is prepared, a solution is obtained which appears saturated but which is always of different strengths. L. Hugounenq, G. Florence and E. Couture (7) announce a solubility of 1.2 g. per liter at 17°C.; J. Kisser (8) mentions a 0.01n solution corresponding to 2.64 g. per liter while others report solutions apparently more concentrated. According to the investigations of R. Dworzak and W. Reich-Rohrwig (9), a 0.01n solution corresponds to a saturated solution. They showed that when picrolonic acid is extracted with cold water for many weeks the solutions obtained are always distinctly weaker than 0.01n. However, if 0.01 molar picrolonic acid is treated with water while frequently stirring on the water bath, allowed to stand overnight, the traces of insoluble residue filtered off (mainly picrolonic acid) and the solution finally diluted to 1000 ml., then a solution (the authors checked the strength with 0.01n sodium hydroxide) very nearly 0.01n is obtained. Probably more concentrated solutions can be prepared; however these are obviously supersaturated because they precipitate picrolonic acid in a short time.

Picrolonic acid forms a number of practically insoluble metal salts. The calcium, lead and thorium salts are especially suited for gravimetric determination. These methods possess a special significance for microanalysis because the precipitate is easily washed free from impurities and because it is possible to dry the precipitate to constant weight in a relatively short time by merely sucking dust-free air through it. Because the precipitate has a high molecular weight, it possesses a favorable conversion factor (the calcium salt, for instance contains 5.64% Ca). Thus the method can determine small quantities with great exactness.

3. *Nitron*, $C_{20}H_{16}N_3$, M.W. 312.36.

This reagent, 1,4-diphenyl-3.5-endanilo-triazolin (4.5), recommended by M. Busch (10), is a derivative of 1,2,4 triazol having the following structural formula:



It is a rather strong base which also exists as a stable salt with carbonic acid. It crystallizes out of alcohol in bright gleaming leaflets or platelets which melt at 189° with effervescence and darkening in color. Nitron is insoluble in water, difficulty soluble in alcohol, but easily soluble in chloroform. Of the salts, the acetate is very soluble in water, but the nitrate and the perrhenate are very slightly soluble—thus, a quantitative determination of these anions is possible (11) (12).

4. *Phenylarsenic Acid,* $C_6H_5 \cdot AsO_3H_2$.

Only zirconium and hafnium are quantitatively precipitated in strong acid solution as normal salts by the reagent. Thus phenylarsenic acid can be used with advantage to determine zirconium.

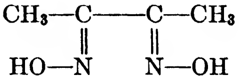
The phenylarsenates of the rare earths are soluble in strong acetic acid solution but thorium salts are insoluble. Thus thorium can be successfully separated from the rare earths in this way.

C. Reagents Which Form Complex Salts

I. INNERCOMPLEX SALTS AS PRECIPITATING AND WEIGHING FORMS

1. *Dimethylglyoxime,*

$C_4H_8O_2N_2$,



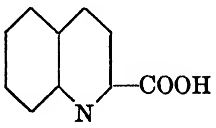
$$\begin{array}{rcccl} \mathrm{CH_3}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{CH_3} \\ & \| & & \| & \\ \mathrm{HO}- & \mathrm{N} & & \mathrm{N} & -\mathrm{OH} \end{array}$$

M.W. 116.08

This reagent was introduced into analytical chemistry by L. Tschugaeff (13). O. Brunck (14) proposed methods for separating nickel from the other monoxides of the ammonium sulfide group. The reagent with its diversified usefulness for determining and separating nickel is undoubtedly well known since it is found in every analytical chemistry text book. Thus a detailed discussion is omitted here. It suffices to mention that it is also possible to use the reagent in micro analytical determinations—R. Strebinger was probably the first to do this (15). The technique of Strebinger using a Pregl filter tube is seldom used now, but has been replaced by the microfilter beaker of Emich.

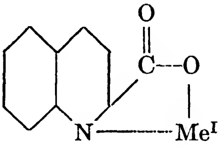
2. *Quinaldinic Acid,*

$C_{10}H_7O_2N$,

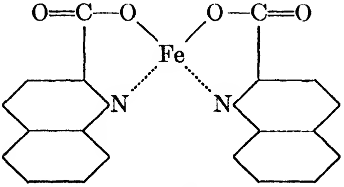


M.W. 173.0

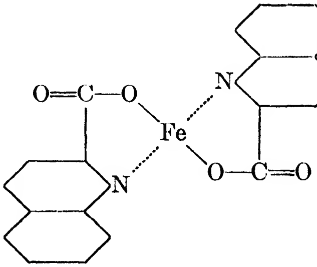
This acid (melting point 155–156°) is recommended by P. R. Rây and M. K. Bose (16) as a reagent which forms innercomplex salts with copper, lead, silver, cadmium, zinc, manganese, nickel, cobalt and iron (II) and which forms basic salts with iron (III), uranium, aluminum, chromium, beryllium, and titanium. The innercomplexes probably have the following structural formula:



No direct experimental evidence for this conception exists, yet consideration of the following facts make it most probable: The quinaldinic acid contains the same atom grouping (=N—C—C—O—) as 8-hydroxyquinoline (oxine) which, as is well known, forms innercomplex salts. Therefore it follows, if only because of analogous reasoning, to assume that compounds with quinaldinic acid do form innercomplex salts. The following properties of the ferrous compound offer further proof of this theory: If ferrous ions are precipitated in the cold with quinaldinic acid, a dark red, seemingly soluble salt is obtained. However the salt, especially on warming, is rather quickly transposed to a blue-violet, practically insoluble modification. This phenomenon becomes understandable by supposing that a complex with a four coordination valent iron in a plain arrangement exists. As a result there is a possibility of a cis or trans form:



Cis (red)



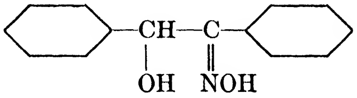
Trans (violet)

The classification of the cis form for the red compound is made because of its instability and because of the impossibility to isolate it. Since trans forms are generally more stable it is necessary to suppose that the violet modification is the transconfiguration.

The sulfuric acid solution of quinaldinic acid is, in the absence of iron and zinc, a specific reagent for copper since then only the copper salt is insoluble in dilute sulfuric acid.

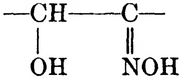
3. Benzoin Oxime,

$C_{14}H_{13}O_2N$,



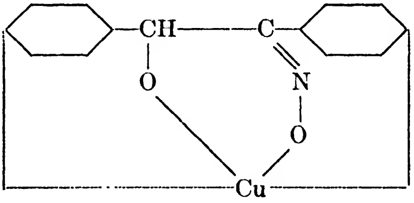
M.W. 227.1

In benzoin oxime we meet the copper specific group,



$$-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\underset{\substack{\|\\ \mathrm{NOH}}}{\mathrm{C}}- \qquad (17)$$

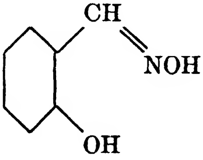
which all acyloin oximes possess. The placing of this reagent into the class of compounds which form innercomplexes is not wholly correct since acyloin oximes form salts which are not accepted as innercomplex salts with certainty. However, it is very probable that the aromatic residual affinity in the benzoin oxime has bound the copper through covalence. As a result it is given the character of an innercomplex salt.



Benzoin oxime is a suitable reagent to detect and determine very minute quantities of copper. However it is not wholly specific for copper since in acetic acid solutions buffered with acetate or even in 20% sulfuric acid solutions molybdenum is quantitatively precipitated.

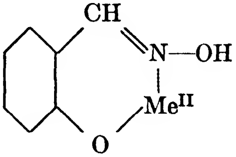
4. Salicylaldoxime,

$C_7H_7O_2N$,



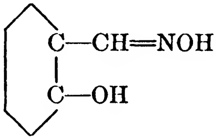
M.W. 137.1, M.P. = 52°

Salicylaldoxime, recommended by F. Ephraim (18) as a specific reagent for copper, forms innercomplex salts of the type:



(19) (20) (21)

The specific group in salicylaldoxime differs from the usual copper specific group of the acyloinoximes in that an extra carbon atom lies between the NOH and OH groups:



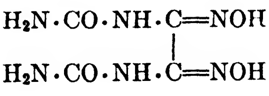
The atom grouping, $HO{-}C{-}C{-}C{=}NOH$ is not in itself specific for copper as corresponding experiments carried out by Feigl and Bondi (21) on aliphatic compounds have shown. From this, it can be concluded that the decisive factor for the specificity of the reagent, $HO \cdot C_6H_4CH{=}NOH$, is the difference in the steric structure brought about by the aromatic binding. The acid concentration is also of importance.

With the exception of the copper salt, all the metal salts of salicylaldoxime are easily soluble in acids. However if the cobalt or nickel salt is once precipitated, they can be dissolved by acids only with much difficulty; but if the precipitation is carried out from the beginning in an acid solution, then only the copper salt is precipitated.

The commercial reagent is used in a dilute aqueous alcohol solution. In preparing this solution, care should be taken to keep the temperature below 80°C. Otherwise, decomposition products are formed which are very difficult to wash out of the precipitate and which cause considerable decomposition during the subsequent drying.

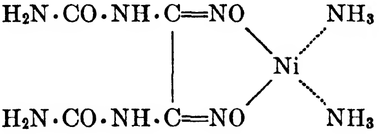
5. Oxalene-diuramino-oxime, $C_4H_8O_4N_6$, M.W. 204.3.

As the formula



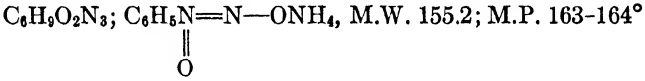
$$\begin{array}{l} H_2N \cdot CO \cdot NH \cdot C{=}NOH \\ \qquad\qquad\qquad\quad | \\ H_2N \cdot CO \cdot NH \cdot C{=}NOH \end{array}$$

shows, this compound contains the nickel specific group. It should be expected that the nickel oxalene-diuramino-oxime must have a structure analogous to the nickel dimethylglyoxime. But actually, it has been shown that the reagent acts as a dibasic acid and forms normal salts. The nickel salt forms, however, an addition compound with ammonia: (22)



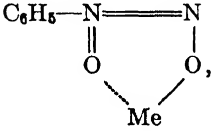
The advantage of the reagent is its solubility in water.

6. Cupferron, Nitrosophenylhydroxylamine Ammonium,



$C_6H_9O_2N_3$; $C_6H_5\underset{\underset{O}{\|}}{N}{=}N{-}ONH_4$, M.W. 155.2; M.P. 163-164°

This reagent, first recommended by Baudisch (23) and which was considered specific for iron and copper, forms innercomplex salts of the following structure,



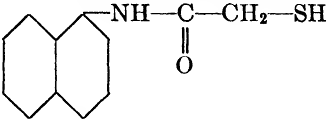
with iron, copper, zirconium, thorium, niobium, tantalum, vanadium and tin, in acid solution.

The salts are soluble in ether, the iron salt very soluble, the copper salt only slightly. The solubility in ether is proof of their innercomplex character. The aqueous acetone solution of the reagent is not changed by hydrogen sulfide; likewise, 2N hydrochloric acid in the cold has no practical effect. When warmed, decomposition takes place with the formation of nitrosobenzol, $C_6H_5 \cdot NO$. When treated with ammonia and sodium carbonate, the iron salt is relatively stable, while on the other hand, sodium hydroxide decomposes it with the formation of nitrosobenzol and ferric hydroxide.

The copper salt precipitates from a weakly acidic copper solution in a white gray flock and is soluble in ammonia with a deep blue color. It is obtained in small blackish-grey crystals by evaporating off the ammonia.

Cupferron has proven itself excellent for many different separations; however, the complex is of no use as a weighing form.

7. Thionalid, Thioglycolic Acid-β-Amino-naphthalide,



M.W. 217.1

M.P. 111–112°

According to the announcement of R. Berg and O. Roebling (24) (25), thionalid appears as white to delicately ivory-colored needles and is insoluble in most organic solvents. Concentrated sulfuric acid dissolves it in the cold, destroys it when hot. When concentrated nitric acid is added in the cold, an oil is formed which reacts vigorously with the nitric acid after several minutes. Ammonium molybdate in acid solution becomes blue; phosphotungstic acid in alkaline solution acts in the same manner. The thionalid reacts with iodine solution to form a very difficultly soluble, crystalline diathionalide:

$$2C_{12}H_{10}ONSH + 2I = C_{12}H_{10}ONS{-}SNOC_{12}H_{10} + 2HI$$

The reagent can be removed from the filtrate in this way since no occlusions or adsorptions are encountered.

Through suitable reactions of the solution the different precipitations with thionalid can be made specific. Ag, Au, Cu, Hg, Sn, As, Sb, Bi, Pt, Pb are precipitated from acetic acid solutions and Cd, Pb, Ni, Co, Mn, Tl from acetic acid, neutral or alkaline solutions. From solution containing ammonium tartrate only Tl comes down as a lemon yellow, crystalline precipitate. This reaction is specific for Tl within the ammonium sulfide group and specific in solutions which contain cyanide and ammonium tartrate in the presence of all metals. (Compare with statements on page 6.)

The metals of the hydrogen sulfide group with the exception of Cd and Pb precipitate better in mineral acid solutions.

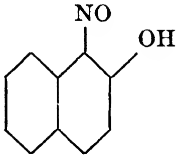
The analytical use of the precipitant is essentially simple since the precipitate can be directly weighed after drying at 105°. Also the determination can be carried out iodometrically since the reaction: $2C_{12}H_{10}ONSH + 2\,I = C_{12}H_{10}ONS{-}SNOC_{12}H_{10} + 2HI$ takes place quantitatively.

There remains to be mentioned the possibility of the colorimetric determination based on the reduction of phosphotungstic acid by the thionalid.

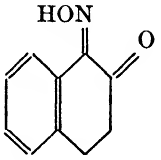
Finally, the precipitate can also be ignited to the corresponding oxide.

8. α-Nitroso-β-naphthol,

$C_{10}H_7O_2N$;



or



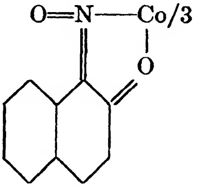
This reagent first recommended by M. Ilinski and G. von Knorre (26) is probably the first organic reagent to be used in quantitative analysis.

The reagent forms an inner complex with cobalt salts of the following formula, $(C_{10}H_6ONO)_3Co \cdot 2H_2O$. Thus the cobalt is obtained in a tri-valent form. This compound is obtained by precipitating divalent cobalt salt solutions with the reagent. In so doing the nitrosonaphthol is reduced to compounds whose nature is so far not explained. These reduction products cause slight traces of cobalt (II) nitrosonaphthol to be formed in the precipitate so that the pure compound is never obtained when cobaltous salts are precipitated. According to C. Mayr and F. Feigl (27), the precipitation of soluble cobaltic salts with the reagent always forms salts of constant composition. The precipitation of cobalt out of a solution of sodium cobaltinitrate, $Na_3Co(NO_2)_6$ forms a purple red precipitate of pure cobaltic nitrosonaphthol immediately. In this case the reaction

$$Co(NO_2)_6''' \rightleftharpoons Co''' + 6NO_2'$$

occurs after forming $Co^{\cdots}$ ions. Since the $Co^{\cdots}$ concentration in the strong complex anion, $(Co(NO_2)_6)'''$ is very minute, it is possible to carry out the precipitation in extreme dilution. This is known to be the most suitable condition for forming the purest precipitates in an easily filterable form. For the same reason it is not possible to make use of these conditions for quantitative precipitation of the cobalt nitrosonaphthol compound, since in this case precipitation is never complete. However, if hydrogen peroxide and sodium hydroxide are added to a solution of a cobaltous salt, and the cobaltic hydroxide formed dissolved in acetic acid, then a complex trivalent cobalt acetate is formed which permits the quantitative precipitation to proceed in a faultless manner.

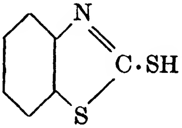
The purple-red precipitate is insoluble in acid, but in spite of this, a weakly acid, neutral or ammoniacal solution is necessary for successful precipitation because the cobaltic nitrosonaphthol is derived from the tautomeric quinoxime form of the reagent. Both of these tautomeric forms are in equilibrium, but in strong acid solution the equilibrium shifts strongly to the phenol form. On the other hand, in weak acid solutions the quinoxime form predominates, and gives an inner complex with cobalt (III) salts of the following structure:



The reagent is suitable for determining cobalt and nickel as well as to separate them from zinc and aluminum.

9. Mercaptobenzthiazol,

$C_7H_5S_2N$,

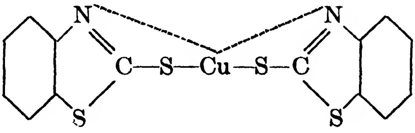


M.W. 167.2

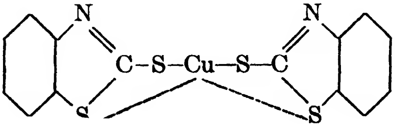
M.P. 180°

Mercaptobenzthiazol (28) has been on the market for some time as a technical product ("Vulkacit-Mercapto," "Kapax"). By many repeated precipitations of the sodium carbonate solution with hydrochloric acid, the pure product is obtained. When an alcoholic solution of the mercaptobenzthiazol is added to an aqueous copper solution which may be neutral, ammoniacal, or weakly acid with acetic acid, an orange-yellow precipitate insoluble in water is formed. It has the composition of 1 Cu:2 thiazol.

The composition and the color of the precipitate make it probable that it is an inner complex salt of the formula



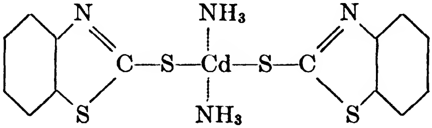
or



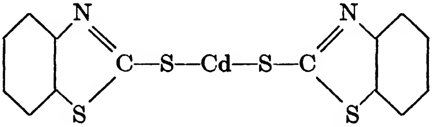
In acid solutions the reaction is specific for copper and makes possible its separation from cobalt, nickel, manganese, zinc, cadmium, the alkaline earths, magnesium and the alkalies. Lead, bismuth, mercury, silver, gold and thallium on the other hand form similar precipitates.

Cadmium is also precipitated out of an ammoniacal solution by an ammoniacal mercaptobenzthiazol solution.

Contrary to expectations, the cadmium precipitate is not an inner complex salt but an ammoniakate



which gives up its ammonia quantitatively when warmed to 110–120° and is changed into a simple salt—



The complex salts of lead, thallium, bismuth and gold can likewise be used with good results for determining these metals. Lead forms two kinds of salts with mercaptobenzthiazol, a normal yellow salt, $(C_7H_4NS_2)_2Pb$, and a white basic salt, $C_7H_4NS_2Pb \cdot OH$. The normal salt is obtained by precipitating the lead with an ammoniacal solution of mercaptobenzthiazol in the cold. However it is always contaminated with the basic salt. If the normal salt is boiled with conc. ammonia, then it is completely changed into the basic form. When an ammoniacal reagent solution is added to a hot, neutral solution of some lead salt, the basic salt comes down as a white needle-shaped, crystalline precipitate which becomes slightly yellow on drying at 110°.

The thallium, bismuth, and gold salts are of normal composition. However, the bismuth salt is contaminated with hydroxide, thus it can not be directly weighed but the precipitate must be ignited to the oxide. Similarly the gold salt is ignited to metallic gold.

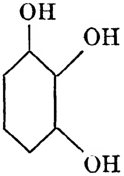
Because the transition of the copper and bismuth salts to the corresponding oxide is absolutely necessary, this precipitation method loses the conversion advantage which the formation of a heavy complex possesses. There is still another objection against the ignition to the oxide: By decomposing the copper mercaptobenzthiazol there is surely copper sulfide or copper sulfate formed. If the decomposition should be carried out so only copper sulfide is formed, it is, as shown by the careful work of L. Springer (29), never possible to obtain a completely sulfate free copper oxide. Thus the results are always too high.

The investigations of Springer have brought out that theoretical results can be obtained by experimentally determining the SO_3 content of the copper oxide and correcting the results. But if it is necessary to take into account these corrections then the method loses the advantage of rapid operation.

The method, however, renders good service where it depends on the separation of copper from cadmium. However there is also a certain limitation here, since other metals, which are precipitated by an ammoniacal mercaptobenzthiazol solution, or which form insoluble hydroxides with ammonia, must first be removed.

10. Pyrogallol,

$C_6H_3(OH)_3$,

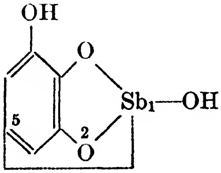


M.W. 126.05

M.P. 132°

Pyrogallol forms complex salts with antimony (30) and bismuth (31) which are well suited for their quantitative determination as well as their separation from arsenic or from lead.

The structure of these compounds is doubtless explained in the sense of inner complex salts. For example, the following formula can be constructed for the antimony compound:



A short summary of the reasons for assuming the above formula follows: The formation of a five membered ring is very probable from analogous reasoning since every five membered ring is known to be especially favorable for the formation of stable inner complexes (1).

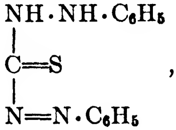
The existence of antimony in a four coordination valent form follows logically from the existence of the halogen double salt of antimony

(III) chloride. The work of S. Hilpert and L. Wolf (32) has proven the ability of the antimony to add itself to compounds with C=C double binding (aromatic hydrocarbon) forming colored addition products of the hydrocarbon used.

The well known property of pyrogallol to react with oxygen forming a brown oxidation product makes necessary in practical determination procedures to always prepare the reagent solution shortly before use and to use well-boiled—thus air free—distilled water.

To test the purity of the reagent, which is recommended, two principal properties are considered: 1) the determination of the melting point, and 2), when a large quantity (about 1 gram) of the reagent is ignited in a weighed platinum or quartz crucible, no weighable residue should remain.

11. Diphenylthiocarbazone "Dithizon,"

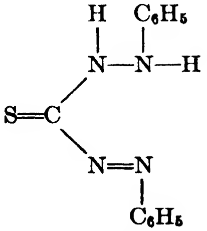


$$\begin{array}{l} NH\cdot NH\cdot C_6H_5 \\ | \\ C{=}S \\ | \\ N{=}N\cdot C_6H_5 \end{array}$$

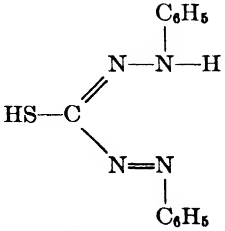
, $C_{13}H_{12}N_4S$, M.W. 256.2

Dithizon, introduced into analytical practice by Hellmut Fischer (33), occupies a special place in the reagents so far discussed. The properties of the different metal dithizonates, and especially the established inner complex character of these dithizonates, gave rise to the working out of new methods. The knowledge obtained by a thorough study of the complex dithizonates and, too, the varied uses made possible by the reagent make a thorough discussion of dithizon necessary, even though it is of little use as a precipitant.

Dithizon forms characteristically colored compounds with many metals which shows typical inner complex salt character (34). For their constitution, it is of value to observe that certain dithizonates can exist in 2 tautomeric forms. It now appears obvious, in analogy to thiourea, to suppose an unknown enol form of the dithizon:



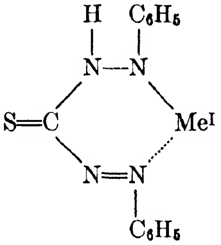
Keto form



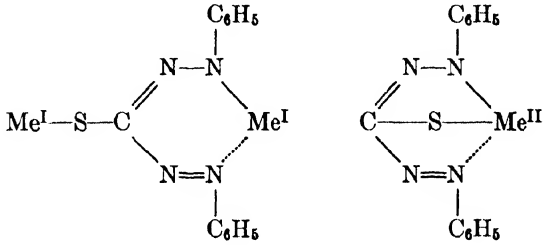
Enol form

For the stable complex keto form the most probable formula is that of a six membered ring. In this case, the metal replaces the hydrogen of the imide group and is bound coordinatively to the double bonded nitrogen by the phenyl residual affinity. In the enol form, which has twice as much metal as the keto form, the hydrogen atom of the sulfhydryl group may also be replaced by metals.

For divalent metals a sulfur connection from the carbon to the metal is possible.



Keto form



Enol forms

The inner complex nature of most of the dithizon compounds is very probably the reason for their solubility in organic solvents. Thus it appears very probable that the dithizon compounds of silver and gold, insoluble in organic and aqueous solutions, are not inner complex salts.

The keto forms are stable in acid or neutral solution. They possess the formulae $Me^{I}D$, $Me^{II}D_2$, $Me^{III}D_3$ (D = Dithizon molecule − 2 H atoms). The enol forms correspond to the formulas $Me^{I}D_2$ and $Me^{II}D$ and are formed from the keto form by treatment with alkali according to the equation: $Me^{II}(DH)_2 + 2OH' = 2Me^{II}D + 2H_2O + D''$, whereby the free valent dithizon forms a dissociable salt in water. The transition of the enol form into the keto forms occurs under the influence of mineral acids:

$$Me^{II}D + D'' + 2H^{\circ} = Me^{II}(DH)_2 .$$

Keto compounds exist for all metals which are at all capable of forming inner complexes with dithizon. Enol complexes are formed principally with the metals of the first five groups of the periodic system. A preview of the reaction of the metals of the several groups of the periodic system with dithizon is given in Table 1.

TABLE 1

I		II		III	IV	V
E	K	E	K	K	K	K
CuD Ag_2D (Au_2D)	CuD_2 AgD (AuD)	...... (CdD) HgD	ZnD_2 CdD_2 HgD_2	. . . . ? (TlD)	? (SnD_2) PbD_2	.... BiD_3

VI	VIII				
K	K	E	K	E	K
(MnD_2)	(FeD_2) (CoD_2) (NiD_2)	. ... (PdD)	. . ... . (PdD_2)	. . .... (PtD)	. ... PtD_2

E = enol compounds.
K = keto compounds.

All the keto complexes are important analytically since they contain twice as many dithizon molecules for a metal atom as the enol compounds. The keto complexes are in general very soluble in carbon tetrachloride; these compounds are distinguished by intensive colors.

The rule exists, that the color tones are changed over with increasing atom radius of the metal from violet over to orange, yellow, then to red.

Ni, Co, Cu, Zn, Sn	Ag, Au, Bi, Hg	Cd, Pb, Tl
Violet	Orange to Yellow	Red

As was already pointed out, dithizon reacts with many metals, therefore it is not at all a specific reagent. However, by selection of reaction conditions it can probably be made specific or at least the number of possible reactions essentially lessened. In the special part a table of these conditions is given.

A further insight on this subject is necessary, since many masking reagents have importance for detection in qualitative reactions. The most suitable reaction conditions for quantitative determination are presented in detail in the discussion of the separate methods.

For quantitative determination by means of dithizon three methods are generally available: 1) The gravimetric procedure; 2) The volumetric analysis; and, 3) The colorimetric determination. Practical results have been obtained only with the 2nd and 3rd mentioned methods. The gravimetric determination has so many difficulties that this method of determination is no advance in comparison to the usual procedures. The voluminous precipitate tenaciously holds water during drying and decomposes very readily at a temperature close to 100°. Thus the complex must be ignited to the corresponding oxide whereby the advantage of a determination form with a favorable conversion factor is lost. The method is made more difficult by the tendency of the precipitate to explode. Thus the ashing must be carried out under certain conditions. Also the fact should be mentioned that the oxide obtained by ignition is practically always contaminated with sulfide or sulfate formed from the dithizon.

The volumetric dithizon procedure is based on the principle of "extractive titration": the metal to be determined is quantitatively extracted out of the aqueous solution by a dithizon solution of known titer. The endpoint is shown by the first noticeable excess of reagent which causes a color change in the carbon tetrachloride layer. From the amount of the dithizon solution used, the unknown metal quantity can be calculated since the dithizon solution was standardized with a solution of known metal content.

These procedures are made possible by the favorable equilibrium circumstance between the aqueous and carbon tetrachloride phases. Since the dithizon as well as the metal dithizonate is practically insoluble in water, but easily soluble in carbon tetrachloride, the equilibrium shifts very strongly in favor of dissolving both materials in carbon tetrachloride.

Since the necessary color reaction for the observation of the titration is completely shown in the carbon tetrachloride phase, the titration is not disturbed by the possibility of color in the water solution.

Often the use of an indirect titration procedure is pointed to. This is especially true if the transition point of the unknown metal is not very clear, or if the reaction does not take place quantitatively in neutral solution. H. Fischer has announced two methods for the indirect titration method:

1. Determination of metals existing exclusively as keto complexes, or whose keto complexes change slowly into the enol form.

The determination is carried out according to the following principles. The metal is shaken out with an excess of dithizon solution of known titer and the carbon tetrachloride solution of the metal dithizonate is freed from the reagent excess by washing with a very weak alkaline solution. (KCN solution for Pb, very dilute NH_3 solution for Cu and Ag). The metal dithizonate is decomposed by mineral acid and the dithizon formed united with a measured excess of silver solution. The metal excess remaining is back titrated with a standardized dithizon solution.

2. Determination of metals whose keto complex is easily changed over into the enol compound.

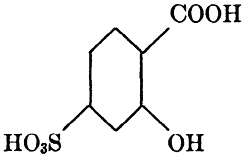
A measured volume of dithizon solution of known titer is extracted in acid solution. That is, sufficient reagent solution is measured out so that a definite excess exists. This excess is now measured in an indirect way by treating it with a known excess of silver and determining the metal excess by titration with dithizon. The colorimetric determination is based on either direct comparison of the carbon tetrachloride solution of the complex with one of known concentration or if this procedure is unsatisfactory, the green solution of dithizon which remains after shaking the complex with dilute acid may be directly compared with a dithizon solution of known content.

The extraction reactions are superior to the other analytical procedures because of their sensitivity and their concentration limit. The sensitivity is close to, and in some cases even greater, than that of spectral analysis. This high sensitivity can in many cases be disturbing; but, by increasing the concentration of the reagent solution and by increasing the volume, this effect can be corrected. The concentration limit lies, in general, between 10^{-7} to 10^{-8} cm^3.

Naturally the high sensitivity makes necessary very pure reagents. Thus it is necessary to prove not only the purity of the reagent itself but it is also necessary to use double distilled water, distilling the second time in glass in order to remove with surety all copper traces.

Perhaps for this reason it is not always possible to reproduce the determinations announced by the authors with equal exactness.

12. Sulfosalicylic Acid,



, $C_7H_6O_6S$ M.W. 218.12

Sulfosalicylic acid, easily obtained by sulfonating salicylic acid, forms, as already mentioned earlier, soluble complex salts which differ in their reactions with other reagents. According to the publications of L. Moser and his co-workers (35), (36), (37) separations utilizing this reagent can, especially in mineral analysis, be used successfully to produce correct results with more facility.

Concerning the reagent itself, it should be pointed out that it appears to be impossible to obtain completely ash free sulfosalicylic acid. The product obtained by purifying the lead salt, recrystallizing it several times, and subsequent destruction with hydrogen sulfide, has 0.05% ash which consists of PbO plus CaO.

Commercial acid has an ash content of 0.1% as a maximum; it contains only traces of Fe and somewhat more Ca and Mg. It is recommended, therefore, to determine the ash content of every preparation before its use. According to an investigation of Ph. Horkheimer (38), the melting point announced in the literature at 108–113° is correct only for preparations of normal moisture content.

In preparations which were dried in a desiccator for six hours over concentrated sulfuric acid, no change was observed during the melting point determination until about 200°. This result is obtained only when the melting point determinations are carried out immediately after removal of the preparation from the desiccator. On standing a short time in the air, the dry acid takes up sufficient water so that at 110°C., incomplete melting begins.

II. PENETRATION COMPOUNDS AS PRECIPITATING AND WEIGHING FORMS

Certain organic bases, such as ethylenediamine, propylenediamine, pyridine, quinoline, oxyquinoline and naphthoquinoline form penetration compounds with metal halides (chloride, bromide, sulfocyanide) of the general formula $(\text{Me. organ. base})_m X_n$. These complexes are decomposed by acid with the exception of the ones formed with naphthoquinoline. In strong mineral acid solution, and in the presence of halogen ions, the α as well as the β naphthoquinoline (39) form practically insoluble precipitates with a limited number of metals. Here the metal halogen acid forms salts of the corresponding base.

Ethylenediamine (40), propylenediamine (41) (42), pyridine (43), benzidine (44) and tolidine (44) together with sulfo-cyanide ions form insoluble salts of the corresponding metals. These salts have proven themselves analytically useful.

Concerning the reagents themselves, only thiourea is discussed here. Further discussion of the more important reagents is presented in the part especially allocated to the discussion of the methods.

13. Thiourea, $CS(NH_2)_2$, M.W. = 108.17

The investigations of Mahr (45) have shown that thiourea is a typical form of amine complex. In contrast to ammonia and other amines (ethylenediamine, benzidine, tolidine) the penetration complexes of thiourea are formed with a large number of metal ions in acid solution.

Such a complex forms either an insoluble compound with an inorganic anion, for example, $2Pb(NO_3)_2 \cdot 11CS(NH_2)_2$ (46), or the penetration complex reacts with a complex inorganic anion—

$$[Cd(CS(NH_2)_2)_2]\left[Cr\begin{matrix}(CNS)_4\\ \\(NH_3)_2\end{matrix}\right]_2^{*} \qquad (47)$$

This compound is a non-electrolyte which is shown by the solubility of the complex in acetone.

Thiourea forms soluble complexes with copper or mercury ions which can be used advantageously to mask these elements. Mercury compounds which are difficult to dissolve, i.e., HgI_2, can be brought into solution by means of thiourea.

The stability of thiourea solutions depends on the purity of the thiourea. A 0.1n solution of thiourea recrystallized out of alcohol remains unchanged a long time.

D. Reagents, Which React with the Formation of Insoluble, Metallic Adsorption Compounds

Here there is only one reagent to discuss, tannin, introduced by Schoeller and Powell (48) and used for many separations by Moser and his co-workers (49) (50) (51). Its action as a precipitant depends on the formation of adsorption compounds (52) with the different metal hydroxides. Soluble complex salts are formed with certain metal ions under suitable conditions. Nothing is known as yet, however, it is suspected that they may be inner complex salts.

The formation of the metal adsorption compounds, or the effect of tannin as a precipitant, is nicely explained with the example of aluminum and beryllium (49).

If one adds a weakly acid or neutral aluminum solution to a saturated ammonium acetate solution which contains at least 3% tannin, then a voluminous, bright brown precipitate is thrown down which coagulates during heating. Beryllium ions are not precipitated under these conditions.

The formation of the aluminum precipitate can now be explained as follows: The addition of a large amount of acetate ion to an aluminum

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[*] The complex forming anion is "Reinecke's salt," $X[Cr(CNS)_4(NH_3)_2] \cdot H_2O$.

salt solution forms a colloidal aluminum hydroxide in highly dispersed form. This positively charged aluminum hydroxide sol shows a great tendency to act as an adsorbent. At the same time the negatively charged tannin sol also acts as adsorbent for the $Al(OH)_3$ sol, forming a practically insoluble adsorption compound, $Al(OH)_3$-tannin. The amount of tannin taken up at different temperatures is not the same, which seems to prove that an adsorption equilibrium really exists here. This equilibrium quickly adjusts itself at higher temperatures in favor of the formation of adsorption compounds. That only aluminum is precipitated under these conditions is evident from the solubility of the beryllium hydroxide in ammonium acetate-tannin solution. The different action of $BeSO_4$ or of $BeCl_2$ and $Be(NO_3)_2$ solutions is considered in a more detailed manner in the discussion of the precipitation methods.

Relative to further publications on the use of tannin, in the third part of the recently published monograph of W. R. Schoeller (53) a bibliography is found.

SPECIAL PART

A. PRACTICALLY INSOLUBLE NORMAL SALTS OF ORGANIC ACIDS AS DETERMINATION FORMS

I. Anthranilic Acid

Preparation of the reagent (6): 3 g. of acid of constant melting point (145°) are dissolved in about 22 ml. of 1N sodium hydroxide, the solution filtered and the slightly yellow filtrate diluted with water to 100 ml. The solution should react very weakly acid to litmus. This is achieved by adding small amounts more of the anthranilic acid. The solution has a very light yellow color and, with difficulty, can be made completely colorless. However the small amount of yellow is not harmful. On the other hand a more brownish solution should be discarded. The solution keeps several months in a tightly stoppered brown bottle which is protected from light.

Ch. Cimerman and P. Wenger (54) recommended that the reagent solution for micro determination be prepared as follows: The analytically pure anthranilic acid is dissolved in 1N sodium hydroxide without excess (for 1 g. acid, almost 7 ml. of 1N sodium hydroxide are needed). After dilution with distilled water the solution is filtered and the pH adjusted to 5.5- 6.5 by means of dilute acetic acid. Distilled water is now added until a 1% solution is present. The pH value of the solution is checked in an aliquot portion with Merck's universal indicator or with the indicator of Chevalier (55).

With anthranilic acid only single determinations can be carried out, since in the neutral, or weakly acetic acid solution most metals with the exception of the alkaline earths and the alkalies form insoluble salts.

INDIVIDUAL DETERMINATION PROCEDURES

1. Zinc Z.

Funk and Ditt (6) give the following precipitation procedure: The zinc solution, which must be free from impurities that would hinder the normal precipitation reaction and which should contain at most only a very slight excess of acetic acid, is diluted to about 150 ml. for each 0.1 g. Zn and then precipitated in the cold by slowly adding 25 to 30 ml. of the reagent solution with stirring. The precipitation is almost complete after about ten minutes and can then be filtered through a porcelain filter crucible. The reagent solution diluted 15–20 times is used as wash solution. The last traces of the precipitate can be easily removed from the beaker by means of a rubber policeman and some alcohol. The precipitate is well dried by suction, washed several times with alcohol to remove the small amounts of sodium anthranilate, again well sucked and then dried to constant weight at 105–110°. This is generally reached after about 30–45 minutes. $F = 0.1937; \log F = 9.28713 - 10$.

The check analyses published by the authors show best agreement with the values of their standard zinc solution. However, a rechecking (56) has brought out that the individual determinations give well checking results when the above directions are exactly followed, but when the actual zinc content of the solution was determined by precipitation as the sulfide, C. Mayr (57) found the results were about 1% too high. Very similar results were obtained by Ch. Cimerman and Wenger (54). According to these authors the error can be avoided by consideration of the following factors:

1. Amount of zinc.
2. Volume.
3. pH of the reagent solution and of the zinc solution to be precipitated.
4. Concentration and amount of the reagent.
5. Amount and concentration of the wash solution.

The determinations when carried out in a Pregl test tube, or in an Emich micro beaker never gave a deviation greater than ±0.3% from the theoretical value.

It is probably most suitable to carry out the precipitation in a weighed porcelain crucible and to filter through a porcelain filter stick. It is recommended to use a porcelain crucible for this purpose because most of the zinc solutions to be determined will probably be acid. Thus the large amounts of acid present can be conveniently removed by evaporation on the water bath.

The following procedure is recommended for the micro determination (54):

To 2–5 ml. of the solution which should contain 1–3 mg. zinc and which should be neutral or very weakly acid with acetic acid (pH 5.5–7), a freshly prepared 1% reagent solution is added dropwise until an excess of 0.3 ml. has been used. The solution is shaken well, allowed to stand for 15 minutes, then filtered through a small filter tube or a small filter stick, washed once with 1–2 ml. of a 0.1% reagent solution and after that

5–6 times with 1–2 ml. portions of alcohol. After the usual wiping out and cleaning of the tube, or of the crucible and the stick, they are dried 15 minutes at 110–115°, as usual wiped with a damp flannel cloth and two buckskin cloths, allowed to stand 15 minutes near the scale, placed on the balance pan for 5 minutes and then weighed in the 20th minute.

To obtain exact results it is absolutely necessary to use no greater excess than 0.3 ml. One must, therefore, in order to determine the exact excess, first carry out a preliminary experiment. In practice, for example, one uses double the quantity of the reagent which is necessary to obtain a complete precipitation. Since here the values are constantly 1% too high the exact amount of reagent necessary can easily be calculated. In the following table a practical example of the calculation is given.

Volume: 2 ml.
Reagent added: 2 ml.
Weight of the ppt: 10.522 mg.
Zinc present: 10.522 × 0.1937 = 2.038 mg. Zn
Zinc present—1%: 2.038 − 0.020 = 2.018 mg. Zn
Theoretically necessary: 0.46 cc. reagent solution for 1 mg. Zn
Theoretically necessary for 2.018 mg. Zn = 2.018 × 0.46 = 0.93 ml.
Excess 0.33 ml.
The whole amount of reagent to use 1.26 ml.

Analogous experiments by Cimerman and Wenger to ascertain the optimum conditions to apply to the macro analysis are not yet published. It is expected that this method will furnish faultless values for macro analysis.

Volumetric determination: The volumetric determination (6) is based on the fact that anthranilic acid in acid solution adds 6 atoms of bromine to each molecule; by determination of the amount of bromine used, the amount of anthranilic acid and thus the zinc present can be calculated. One atom of zinc corresponds to 12 atoms of bromine.

Titration procedure: The precipitate of zinc anthranilate which has been obtained and washed in the above described way, is dissolved in about 4N hydrochloric acid, quantitatively transferred to a bottle with a ground glass stopper and titrated with standard bromine-bromate solution; as indicator, a solution of indigocarmine and styphninic acid (0.2 g. indigocarmine plus 0.2 g. styphninic acid) dissolved in 100 ml. of water is used. Disregarding the precipitate which comes down the solution is titrated until the indicator changes from green to yellow (slight excess of bromine). Now several milliliters of 0.2N potassium iodide solution is immediately added, the solution diluted and the iodine liberated back titrated with thiosulfate using starch as an indicator.

Unfortunately no experiments to check the titration results by the precipitation method of Funk and Ditt, or of Cimerman and Wenger have been made. It is however, to be suspected, that the discrepancies which Funk showed the gravimetric method possessed are also present in the titration method since the error is caused by some anthranilic acid that could not be washed out.

2. Cobalt (6) Co

The solution to be precipitated, which should contain no free acid and which should have a volume of about 250 ml. for 0.1 g. of cobalt, is heated to boiling and precipitated with 15 ml. of reagent solution. For smaller amounts of cobalt the volume of the solution is less and the amount of the reagent lessened correspondingly. After the precipitation the solution is boiled gently for 5 minutes then allowed to stand for 5–10 minutes and filtered through a porcelain filter crucible while still hot. The precipitate is first washed in the cold by a wash solution containing 5 ml. of reagent solution diluted with 95 ml. of water, and at the end several times with alcohol. Since the precipitate is not voluminous, amounts of cobalt of 0.1 g. and more can be satisfactorily determined. The well sucked precipitate is dried to constant weight at 105–110°. $F = 0.17803$; $\log F = 9.25049 - 10$.

The practical use of this method is probably very limited, since the analyst must in almost all cases separate the cobalt from iron, nickel, zinc, etc. Since in these cases the more recent method of C. Mayr and F. Feigl (27), which allows the determination of cobalt in the presence of these metals, is available, cobalt would scarcely be determined in the above mentioned way.

The **volumetric determination** can be accomplished in the same way as announced for zinc.

Microanalytical determination: P. Wenger, Ch. Cimerman and A. Corbaz (58) have also studied the determination of cobalt with anthranilic acid and worked out a micro determination.

Preparation of the reagent solution: 0.2 g. of anthranilic acid (p.a.) are dissolved in 1.6 ml. of 1N sodium hydroxide, the solution diluted with 8 ml. of double distilled water and the diluted solution filtered through a dry filter. 6–7 drops of 5% acetic acid are added to the filtrate making 10 ml. of a 2% reagent solution. This solution has a pH value of 6 which is checked by means of Merck's universal indicator. The solution kept in a brown flask and protected from light remains almost colorless. However, it is necessary to prepare new material after two days standing.

Determination procedure: The neutral or very weakly acid (however acetic acid is to be avoided)* cobalt solution which should contain 0.1–4.0 mg. Co is put in a Jena micro filter beaker and heated on a copper block which is kept at 170° or on an electric hot plate to boiling.

Now the reagent solution is added dropwise until an excess is present—depending on the amount of cobalt present. For 1–4 mg. cobalt, a 90–130% (optimum—115%) excess of reagent is used: that is, 0.5 ml. of reagent solution for each milligram of cobalt.

For 1–0.2 mg. of cobalt an excess of 330–335% is used; that is, 0.16–0.2 ml. reagent for 0.1 mg. cobalt.

For amounts of cobalt less than 0.2 mg. cobalt an excess of 600–770% is used; that is 0.16–0.2 ml. of reagent for 0.1 mg. cobalt.

The solution is shaken, heated until boiling starts and then allowed to stand 10 minutes. It is then filtered, washed once with 2 ml. of 0.2% sodium anthranilate solution and finally twice with 1 ml. portions of alcohol.

The precipitate and the filter beaker are dried at 120–130° on the heated drying block† while dust free air is slowly passed through. After 15 minutes the filter beaker is removed from the drying block, allowed to cool, cleaned as usual with a damp flannel cloth, and then with a dry piece of buckskin. The filter beaker is then placed on a nickel block next to the balance, allowed to stand 5 minutes on the nickel block in the balance, then five minutes more on the balance pan and then weighed in the 25th minute.

The results obtained by the authors are extraordinarily exact.

Weakly acid solutions are neutralized by adding a 1% soda solution until a turbidity arises. This turbidity is again brought into solution by adding 1–3 drops of very dilute hydrochloric acid (1 ml. of conc. HCl in 200 ml. water). Strongly acidic solutions are best freed from the excess acid by evaporation to dryness. The residue is dissolved in water by adding a drop of dilute hydrochloric acid (1 + 200).

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* The determination is in error because of the presence of sodium acetate, that is the results are too low; sodium chloride and ammonium chloride when present in small amounts do not influence the results.

† The drying block for the micro filter beaker is manufactured by the firm, Paul Haack, Wien, IX, Garelligasse 3. Compare also F. Hecht, *Mikrochim. Acta*, **3**, 129 (1939). A universal apparatus for microanalytical purposes. For drying microapparatus and precipitates as well as for evaporations and fuming of liquids.

The authors have also carried out determinations both with a Pregl filter tube and with an Emich filter stick, obtaining good results with both methods*. If it is desired to use a strong acid solution which must be evaporated to remove the excess of acid, then Emich's filter stick is most suitable. The solution is brought into a weighed porcelain crucible by means of the filter stick, evaporated, the solution precipitated as described, the precipitate sucked through the filter stick and finally crucible plus filter stick plus precipitate are weighed.

3. Nickel (6) Ni

The solution, neutral or at most very weakly acetic acid, whose volume should be about 300 ml. for each 0.1 g. nickel, is heated to boiling and precipitated by the dropwise addition of 25 ml. of reagent solution with stirring. After addition of the reagent, gentle boiling is continued for 5 minutes, the solution allowed to stand for 10 minutes and then filtered through a porcelain filter crucible. The precipitate is washed with the same solution used for cobalt and dried to constant weight at 105–110°. F = 0.17742; log F = 9.24900 — 10.

Also the possible use is very limited here, especially since separations cannot be carried out successfully.

The **volumetric determination** procedure is identical to that of zinc; it has proven advantageous to dissolve the nickel precipitate in concentrated, hot hydrochloric acid and then to dilute the solution.

4. Cadmium (6) Cd

The determination procedure is analogous to the procedure announced for zinc. Whether in this case the precipitation is also better when carried out in a 1% reagent solution has not yet been experimentally checked. It is to be expected that the use of the diluted reagent solution and of a determined pH concentration is also very advantageous. F = 0.29225; F = 9.46576 — 10.

The **volumetric procedure** described for zinc is also applicable.

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* According to a private communication from Prof. Wenger, an extensive work on microdeterminations by means of anthranilic acid will appear shortly.

5. *Manganese* (*6*) Mn.

According to H. Funk and M. Demmel (6) the white manganese anthranilate, $Mn(C_7H_6O_2N)_2$, can be used as a precipitant for manganese although the solubility of the salt is considerably larger than the corresponding zinc, cadmium and copper salts. Since the sensitivity of the determination according to the authors is not very great, a detailed description is not given here especially since it is useless for the determination of manganese in the presence of calcium where simple methods of precipitation are applied.

6. *Copper* (*6*) Cu.

The neutral or very weakly acetic acid solution, whose volume should be 200 ml. for 0.05 g. of copper, is heated until it begins to boil. Then the flame is removed and the solution precipitated by adding 12.5 ml. of the reagent solution for each 0.05 g. of copper. After several minutes the precipitate has practically settled. The hot solution is filtered in a filter crucible and washed with hot water containing 1 to 2 ml. of reagent solution for each 100 ml. of water. The precipitate is dried at 105–110° to constant weight. $F = 0.1838$; $\log F = 9.26435 - 10$.

The **volumetric determination** cannot be accomplished in the way already described because of the effect of the copper salt on potassium iodide; however it can be done in the following way: The copper salt is dissolved in 4N hydrochloric acid as described for zinc, titrated with bromate solution and the small bromine excess now determined by arsenic acid.

The hydrochloric acid solution is titrated with bromide-bromate solution until the indicator just changes into yellow. After this a small amount of a standard solution of arsenic acid is added, then some more indicator and now the solution is titrated with bromide-bromate solution. The end point is reached when the indicator changes to green.

7. *Lead* Pb.

In contrast to the precipitates or precipitations so far discussed, the lead anthranilate is amorphous at first, then changes quickly into the crystalline form (four sided leaflets).

Determination procedure (59): 30 ml. of reagent solution are added in the cold to the practically neutral solution whose volume should be about 100 ml. for 0.1 g. of lead. After at least an hour of standing, during which time the amorphous precipitate has changed into the crystalline form, the solution is filtered through a filter crucible, the precipitate washed first with a reagent solution diluted 5 or 6 times, then at the end with a little alcohol and finally dried at 105–110° to constant weight. F = 0.4323; log F = 9.63579 — 10.

For the precipitations discussed so far the presence of ammonium salts were unimportant. Here they cause negative errors in the lead determinations, possibly as a result of the formation of basic salt. Moderate amounts of alkali chloride or nitrate do not disturb the determination.

The **volumetric determination** gives results which are not so exact as those obtained by gravimetric methods. If, in spite of this, it seems desirable to use the volumetric method then the washed precipitate is dissolved in hot 10% ammonia acetate solution, this solution is then acidified with hydrochloric acid and after cooling is complete, the solution is titrated.

8. Mercury Hg.

The determination of mercury (59) gives correct results only if carried out in alkali and ammonia free solutions in the cold and the solubility of the precipitate held to a minimum by quick filtering and washing. This solubility is already a noticeable factor on long standing even in the cold and is especially high in hot solutions. The following **procedure** has been developed taking these difficulties into account.

The solution which must contain the mercury only in the form of the nitrate and which should be as near neutral as possible is diluted to 200 ml. for 0.1 g. of mercury and 10 ml. of the reagent solution are added in the cold. The precipitate which settles quickly and which should not stand more than two minutes at the very longest is filtered through a filter crucible. In order to obtain a quick filtration the precipitate should never be allowed to become dry. The same care is used during the washing of the precipitate using a reagent solution diluted twenty times. By following this procedure the filtration and washing of the precipitate is finished in a few minutes. The precipitate is now dried to constant weight in the usual manner at 105–110°. F = 0.4237; log F = 9.62706 – 10.

The **volumetric determination** gives no satisfactory values.

II. Picrolonic Acid

Of the crystalline salts of picrolonic acid with metals, only calcium (9), (60), lead (61), and thorium (63) have been used for their quantitative determination. Their special value lies in the ease of filtration of the precipitate and the favorable conversion factor. These properties have also brought about the use of the methods in micro analysis; the results obtained are excellent and allow the smallest amounts of the metal to be determined in a more simple way and with the same or more exactness than the methods usually used.

Preparation of the reagent: A 0.01N solution of the picrolonic acid in water prepared according to the directions given on page 9 is used. This solution saturated at room temperature remains clear a long time.

INDIVIDUAL DETERMINATIONS

1. Calcium Ca

The air dried calcium salt has the composition $Ca(C_{10}H_7N_4O_5)_2 \cdot 8H_2O$. The salt has proven to be extraordinarily constant at room temperature, thus by sucking dust free air through the precipitate constant weight is reached in one to two hours. The apparatus sketched below (Fig. I) is best for this purpose.

The solution from which the calcium is determined should be neutral to litmus, should contain not more than about 0.1 g. of calcium and should not have a disproportionately large volume. Alkali and ammonium salts as well as magnesium salts should not be present in the solution in very great excess, however as the authors (9, p. 110f) show in the calcium-magnesium separation, about a tenfold excess of magnesium is not disturbing.

Determination procedure: The reagent solution is added dropwise from a burette to the warm (about 50°) solution in a large beaker until a precipitate comes out. If this is flocculent, then one interrupts the further addition until warming and shaking have changed it into the coarse crystalline form (strongly refractive crystals). The further addition of the reagent follows at a tempo that makes possible new precipitations which are crystalline from the beginning—if possible.

If this should not happen then the addition of the reagent is again interrupted and the precipitate changed into the crystalline form in the way just described. If nothing more precipitates on adding more reagent even in the cold, then picrolonic acid of at least half the volume that the solution now possesses is added and the precipitate allowed to stand several hours in a cool room. The crucible to collect the precipitate is prepared as follows:

The cleaned crucible is dried in the apparatus sketched above by sucking a dust free air stream through it. Constant weight is usually reached after one to two hours.

The supernatant liquid is now decanted through the crucible and the precipitate quantitatively transferred into the crucible which is easily done by means of a rubber policeman. Two washings are sufficient, filling the crucible half full each time with cold water and sucking off.

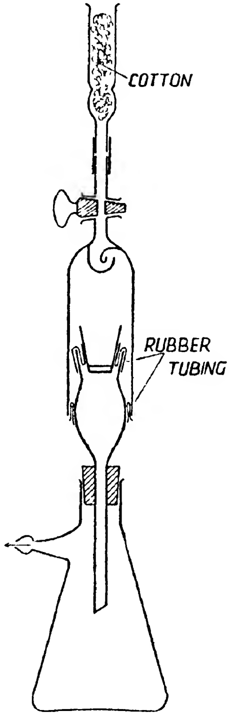

FIG. I

The precipitate is now dried to constant weight in an air stream in the described way. $F = 0.05641$; $\log F = 8.75138 - 10$.

1a. Micro determination: The micro filter beaker of Emich in which the precipitation can take place and in which the precipitate can be weighed is best suited for the micro determination. It is very advantageous in the weighing to use an empty filter beaker of the same dimension as the precipitation beaker since when containers of about the same surface are placed on both balance pans, the errors depending on the adhesion of atmospheric moisture become almost completely eliminated. Pregl has pointed out this error source in his book; the tare bottles that he used however, have the disadvantage that they possess another weighing surface than the object to be weighed. By using counterpoises of the same form it is easier to obtain agreeing results; even with the best microbalances it can be done only under certain conditions.

If the determination of the concentration of a solution is a factor then it is often advantageous, instead of the usual weighing, to pipette the reagent in. For the exact conversion factor the specific weight of the solution is determined. In order to avoid small errors resulting from evaporation during the weighing the filter apparatus is provided with a glass cover as shown in the above figure (Fig. II). In order to saturate the air space of the filter beaker with moisture, the air is saturated several minutes before the weighing with several drops of distilled water. Naturally the tare container is treated in exactly the same way. In this way an error in weight through evaporation and wetting of the inner surfaces of the filter apparatus is, with surety, avoided. If the determination solution is prepared by the exact dilution of a "macro-solution," then as already mentioned, the specific weight is determined and the corresponding volume calculated from the weight. Practically however, the solutions are so dilute that the corrections depending on this factor will hardly be significant.

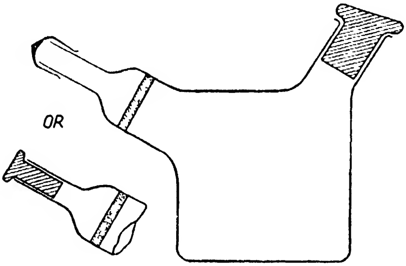

Fig. II

The precipitation itself is identical to the method described for the macro method; the reagent solution is added dropwise through the neck of the container by means of a capillary pipette. After the precipitation is finished, it is allowed to stand for at least an hour in a cool room before filtering. The washing of the precipitate can be accomplished with a surprisingly small amount of water; it suffices to wash twice each time with about 0.2 ml. which can be brought to all container walls by skillful shaking. To dry in a dust free air stream, the neck of the filter beaker is closed with a Pregl dust filter, the filter support brought into vertical position and the air stream aspirated through the container for about half an hour. After the usual cleaning of the outside of the container and after 10 minutes standing on the micro balance, the precipitate is weighed.

1b. Colorimetric determination of calcium: Picrolonic acid and bromine water form turbid solutions which dissolve in alkali with a blood red color. Alten (60) and his coworkers found that the color is approximately proportional to the picrolonic acid content. The procedure is based on the fact that the color of a solution of known content of calcium picrolonate is compared with the color which was obtained with the test solution. For measuring a yellow green filter of optical center 530 mμ is used since here the displacement of the color tone, which oscillates between red and yellow is not noticeable.

Before the determination the excess of bromine must be removed. Iron (III) and aluminum salts are disturbing, but can be held in solution by sulfosalicylic acid.

Determination procedure: 5 ml. of the very weakly acidic solution of the unknown is neutralized in a 10 ml. measuring flask with 2N sodium hydroxide (methyl orange) and several drops of 10% sulfosalicylic acid are added. 1 to 2 ml. of the filtered solution is diluted to a 10 ccm. volume in a centrifuge glass (12 mm.), three times the amount of ice cooled 0.01N picrolonic acid is added and the solution allowed to stand four hours in ice cold water with hourly shaking. It is then filtered through a micro porcelain filter stick BII; adhering picrolonic acid is removed by washing three times with ether. The calcium picrolonate is dissolved in hot water, the solution transferred into a 50 ml. measuring flask and warmed on the water bath with 1 ml. of bromine water. After the addition of 10 ml. of alcohol and slow cooling, 2 ml. more of 2N sodium hydroxide is added and on the next day, the color, which should be protected from light, is compared with the color of a solution of known calcium content prepared in the same way.

According to the announcements of the authors 20–150γ Ca/1 ml. can be determined by quantitative colorimetry.

A difficulty of the method may be in completely washing out the last traces of the picrolonic acid from the calcium picrolonate. In every case it is recommended to wash the calcium precipitate of both the unknown and the standard solution with about the same amount of ether.

In the determination of very small amounts of calcium the calcium content of the sulfosalicylic acid can also give rise to serious errors. Compare with page 25 and page 142 where the ash content of sulfosalicylic acid is announced.

2. Lead (61) Pb.

Lead picrolonate has the formula $Pb(C_{10}H_7N_4O_5)_2 \cdot 1.5H_2O$; the water of crystallization is not lost even at 130 to 140°.

The lead nitrate solution to be precipitated should not contain excessive nitric acid and should react neutral to litmus. Larger amounts of nitric acid are removed by evaporation to dryness on the water bath. Neutralization with bases or ammonia is to be avoided since the solution should contain as little alkali or ammonium salts as possible. The volume of the solution is made up to about 50 ml. for 0.1 g. of lead.

Determination procedure: The solution is heated in a large beaker until boiling begins and for each 0.1 g. of lead 100 ml. of 0.01N picrolonic acid solution are added dropwise with constant stirring. After this, picrolonic acid is added in a stream in half the quantity of the solution and placed in the refrigerator until completely cooled. Then under careful suction, particularly at the start, the solution is transferred into a filter crucible and the precipitate brought quantitatively into the crucible with the least amount possible of ice cold water. The precipitate is washed with ice cold water until the filtrate becomes colorless; about 50 ml. is sufficient. After about $1\frac{1}{2}$ hours of drying at 130 to 140° constant weight is reached.

$F = 0.27249$; $\log F = 9.43535 - 10$.

2a. Micro determination: The determination is carried out in a micro filter beaker (Emich); the volume of the solution should be about 0.5 to 1 ml. for 1 to 5 mg. of lead. Nitric acid solutions are evaporated to dryness to remove the excess of acid. The apparatus sketched above has proven excellent for this purpose (Fig. III).

The filter beaker is fastened in the tube by means of a cork stopper. The ground glass stopper with a fused dust filter extends into the drying chamber and is connected to a water aspirator pump. The solution at 85° can be evaporated in the shortest time by sucking dust free air through it. The residue of the evaporation is dissolved in 0.5–1 ml. of water and the precipitation takes place according to the following directions:

The content of the filter beaker is heated on the electric hot plate until it begins to boil. Then the filter beaker is placed on a boiling water bath that has a cover glass; the water bath announced by W. Reich-Rohrwig (62) for micro analytical purposes where the micro filter beaker is placed in a tube, is still better. Absolutely clear, 0.01N picrolonic acid, is added dropwise to the hot solution from a capillary pipette and after each five drops the beaker is carefully shaken. Special attention should be paid that nothing remains hanging on the tube walls or dries out there. If about 30 drops of precipitant are added for 1 mg. lead, then 15 drops of the reagent are added at once and the beaker allowed to stand 5 minutes more on the water bath with occasional careful shaking after which it is allowed to cool 20-30 minutes in the refrigerator. Although the precipitate usually does not settle completely if the solution shows only a little turbidity, it can be readily filtered. The precipitate is separated from the liquid by gentle suction in the beginning and later under strong suction. It is then washed with a total of 1.5 ml. of ice cold water for 1 mg. lead (divided into 2-4 washings). A graduated "micro wash bottle" (Fig. IV) has proven

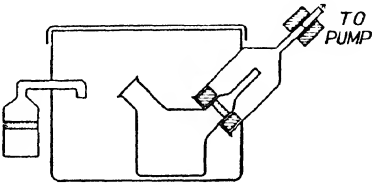

FIG. III

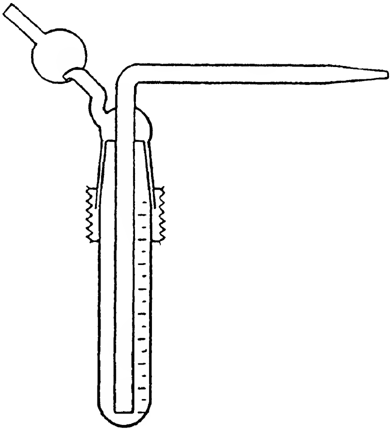

FIG. IV

excellent for this because it permits an upwardly inclined stream to be blown out of the right angled bend of outlet tube. This makes a thorough washing of the inclined inner walls of the beaker during filtration very much simpler. After the washing is finished the precipitate is dried for ¾ hour at 130° preferably sucking through dust free air as already described above.

The results obtained by following these directions leave nothing further to be desired.

The determination also gives, in the presence of not more than a five fold excess of platinum, satisfactory results. This is extremely valuable for quantitative micro mineral analysis since sometimes small amounts of platinum go into solution from the platinum containers used but do not impair the results.

3. *Thorium* (*63*) Th

Picrolonic acid forms a thorium salt of the composition $Th(C_{10}H_7N_4O_5)_4H_2O$, with a thorium content of 17.82%. The thorium picrolonate is far less soluble than lead picrolonate and is especially suited for micro determinations.

Determination procedure: After addition of the picrolonic acid solution the solution should be diluted to about 50–60 ml. for every 10 mg. of thorium and after addition of the precipitant the final volume calculated to contain about 2½ times the amount of picrolonic acid theoretically required; that is, for 10 mg. thorium about 50 ml. 0.01N picrolonic acid is required. The precipitation is accomplished according to the following directions:

The solution is evaporated to dryness in a 250 ml. beaker to remove the free nitric acid, dissolved with the least possible amount of water (about 5 ml. for 10 mg. Th), sufficient acetic acid added so that at the finish of the precipitation 2½ to at most 3% by volume of acetic acid is present, and the solution heated until boiling starts. Now the picrolonic acid is allowed to flow in dropwise out of a dropping funnel under steady, gentle boiling. Soon a crystalline precipitate comes down (under the microscope one sees well formed crystals arranged in a rosette form). When no more new precipitate comes out, the remaining reagent solution can be added all at once. After completion of the precipitation the solution is allowed to cool for at least an hour in the refrigerator and then filtered through a filter crucible. 3–4 washings with several ml's. of ice cold water are sufficient to remove the last traces of picrolonic acid. The precipitate in the crucible is dried with air to constant weight using the apparatus described in the determination of calcium. The time required depends on the amount of the precipitate, however more than 3 hours are very seldom necessary.

$F = 0.1782$; $\log F = 9.25091 - 10$.

3a. Micro determination (63): The micro analytical thorium determination represents, if one excepts the usual (thus far common) ignition of the oxalate to the oxide, the first exact microgravimetric thorium determination. In comparison with the determination as oxide, the new method possesses a far greater exactness.

The adjustment of the precipitation directions to the needs of micro analysis make it appear desirable to choose the conditions so that the precipitation and weighing may be done in an Emich micro filter beaker. Because the filter beaker is of limited capacity (averages about 10 cc.), it is naturally possible only in a somewhat complicated way to reach the optimal (about 55%) concentration of 0.01N picrolonic acid in the solution. As the precipitation procedure given below explains, one must first orient himself by an approximate determination of the amount of thorium to be expected. Thus the method is somewhat time consuming. However, this disadvantage is out-weighed by the exactness obtainable. Thus the somewhat time consuming procedure appears as a whole to be justifiable.

Precipitation procedure: A micro burette which allows a direct reading of differences of 0.01 ml. and an approximation of 0.001 ml. is filled with the thorium solution. Out of this burette the solution is allowed to run into a weighed Jena micro filter beaker which was sucked dry with air beforehand using the apparatus described above. The filter beaker containing the solution is now placed in the apparatus and the solution evaporated to dryness at 85°C in a dust free air stream. Care should be taken that the air stream is not too violent, since loss may occur by carrying through of some liquid droplets onto the sinter plate. The dry residue is dissolved in about 1 ml. of hot water and enough glacial acetic acid is added from a micro pipette of 0.1 ml. divisions so that the acetic acid concentration, which is calculated before filtering the final precipitate, is about 3% by volume. The filter beaker is now placed on the electric hot plate and the contents heated until boiling starts. To avoid boiling over (loss by boiling) the beaker is removed from the hot plate at very short intervals, set back again, etc. To the final solution, about 1.5 to 2 ml. picrolonic acid solution is added from a micro pipette in portions of 0.5 ml. and the solution carefully shaken after each addition and heated on the hot plate until boiling. (With thorium quantities of more than 1 mg. one uses 2.5 ml. of picrolonic acid.) After addition of the precipitant is complete, the beaker is kept gently boiling on the hot plate in the way described. A beautiful crystalline precipitate quickly comes down and leaves the supernatant liquid wholly clear. Now the rest of the picrolonic acid necessary is added. (Altogether 2½ times the theoretical quantity.) If the volume so reached totals more than at most 4 to 4.5 cc. (according to the capacity of the filter beaker) then further addition is interrupted. The available volume of the beaker makes it necessary to evaporate 2 or 3 ml. from the solution at 85° in the way already described and not until then is the rest of the precipitant added. Sometimes a crust of picrolonic acid precipitates out on the inner wall of the filter beaker and must be brought in solution again by warming over a boiling water bath.

If the amount of thorium to be expected has been determined by a rough analysis then the next determination should give the exact value.

To calculate the necessary volume of the precipitant, or to calculate the volume that should be added after addition of the first part of the precipitant, the following procedure is carried out: 1 ml. of 0.01N picrolonic acid solution contains around 2.5 mg. of picrolonic acid, which suffices to precipitate about 0.4 mg. thorium. The volume of liquid in the filter beaker can easily be approximated according to the weight; if the approximate capacity of the beaker is known, it is easy to judge the total picrolonic acid necessary for precipitation and how much should be evaporated in order to have picrolonic acid concentration of about 50%. The accuracy of such an estimation is completely sufficient.

The following example should explain the practical use of the above procedure: To determine about 1.5 mg. thorium the end volume should be 5.0–5.5 ml. Applying the above discussion to this case the 1.5 mg. Th requires 5 times this weight, therefore, about 8 mg. of picrolonic acid, corresponding to almost 3.5 ml. of the 0.01N solution. If the end volume should be 5.5 ml. then there should be in the solution about 3 ml. of unused precipitant. Therefore, before the precipitation of the thorium solution whose volume is brought to 1 ml., 0.16–0.17 ml. of glacial acetic acid (3% for 5.5 ml.) is added and then about 3.5 ml. of reagent. After this about 2–2.5 ml. are evaporated and 3 ml. more of precipitant added. With very small amounts of thorium (1.4–0.5

mg.) precipitation can be carried out without evaporation of any part of the liquid.

The results leave nothing to be wished for.

III. Nitron Nt.

1. Determination of Nitric Acid as Nitron Nitrate (10) (11)

Preparation of the reagent solution: 10 g. of commercial Nitron is dissolved in 100 ml. of 5% acetic acid. The intensively red colored solution is filtered through a porous glass filter crucible to remove the small amounts of resinous impurities. When kept in a dark flask, the solution remains unchanged for a long time.

Determination procedure: 10 drops of dilute sulfuric acid are added to the unknown which contains approximately 0.1 g. of nitric acid in 80–100 ml. of water. The solution is heated to boiling and 10–12 ml. of reagent solution added in a stream. After standing an hour and a half to two hours in ice water, the Nitron nitrate settles to the bottom of the beaker in very fine needles which have a brilliant, silky appearance.

The light yellow supernatant liquid is now poured through a Gooch-Neubauer platinum crucible, or if such a crucible is not available, through a glass or porcelain filter crucible, then the precipitate is washed into the crucible with the original liquid (mother-liquor) and the precipitate, well sucked. After this it is washed with 10–12 ml. of ice water using small portions and again well sucked. The precipitate is dried to constant weight at 110°. Generally no longer than $\frac{3}{4}$ of an hour is necessary.

$F = 0.1679; \log F = 9.22498 - 10.$

The determination cannot be carried out in the presence of the following ions: Br', I', NO'_2, CrO''_4, ClO'_3, ClO'_4, ReO'_4, since the corresponding Nitron salt is more or less insoluble. Some of these ions can be destroyed using the following method:

Br': Chlorine water is added dropwise to the neutral solution with heating until no yellow color arises.

I': Potassium iodate is added in excess to the neutral solution, the solution acidified with acetic acid and heated until the precipitated iodine is dispersed. The iodic acid has no influence on the determination since Nitron iodate is very soluble in water.

NO'_2: The concentrated solution (0.2 g. material in 5–6 ml. of water) is allowed to drop through pulverized hydrazine sulfate.

CrO''_4: These ions may be reduced in a similar way with hydrazine sulfate.

In spite of the unfortunate solubility of Nitron nitrate in weakly acidified water (about 9.9 mg. in 100 ml. of water at the usual temperature) the results of the determinations are very rarely too low. It must, therefore, be supposed that the Nitron nitrate contains some occluded Nitron acetate which compensates for the errors arising through incomplete precipitation. L. W. Winkler (64) found on examination that the amount of ice water recommended for washing was insufficient and published the following method for the determination:

The neutral solution of about 100 ml. volume containing at most 0.05 g. and at least 0.01 g. NO_3 is acidified with 1 ml. of acetic acid, warmed to 60-70° and then 10 ml. of completely clear reagent solution is added. After allowing to stand 24 hours in the dark, the precipitate is collected on a small cotton pad in a funnel and washed with 50 ml. of saturated Nitron nitrate solution; the last portion of wash water is quickly sucked off. The precipitate is dried 2–3 hours at 100°. The investigations of Winkler have shown that the presence of large amounts of sulfuric or iodic acid have almost no disturbing effects. On the other hand, in the presence of chlorides the results are always somewhat too high. Since the errors are rather constant, the following corrections depending on the weight of the precipitate may be applied.

Weight of Precipitates	Cl in 100 ml.			
	0.0 g.	0.1 g.	0.3 g.	0.5 g.
0.30 g.	+0.4 mg.	−2.0 mg.	−4.4 mg.	−6.8 mg.
0.20 g.	+0.8 mg.	−1.2 mg.	−3.0 mg.	−4.8 mg.
0.10 g.	+1.2 mg.	−0.2 mg.	−1.5 mg.	−2.8 mg.
0.05 g.	+1.4 mg.	+0.2 mg.	−0.8 mg.	−1.8 mg.

In addition, the investigations of Winkler have shown that the solubility of Nitron nitrate in water is higher than was announced above. At 20° for instance, 37.1 mg. of Nitron nitrate are dissolved by 100 ml. water after standing at this temperature 24 hours. If, however, a solution saturated at a warmer temperature is cooled to 20° and allowed to stand 24 hours at this temperature, then 53.1 mg. of the Nitron nitrate are dissolved by 100 ml. of water. The corresponding amount dissolved at 0° is 21.13 or 33.7—depending on the method. However, this solubility is very greatly decreased by the addition of Nitron acetate: if 10 ml. of Nitron acetate solution is added to 100 ml. of Nitron nitrate solution saturated at 17.5° then the solubility after 24 hours is found to be only 2.0 mg. Nitron nitrate.

2. Determination of Rhenium as Nitron Perrhenate (12)

The crystalline Nitron perrhenate, in the presence of sufficient excess of precipitant, offers an excellent way of determining ReO'_4 ions because of its small solubility.

Solubility of Nitron Perrhenate at 0°C.

(a) in pure water . ... 0.017–0.018 g./100 ml.
(b) in a 0.3–0.5% Nitron nitrate solution 0

For precipitation a 5% Nitron acetate solution prepared by dissolving 5 g. of commercial Nitron and 3 ml. of glacial acetic acid in 100 ml. of water is used. Since the removal of small amounts of resinous impurities cannot be done with a paper filter, the solution is sucked through a filter crucible shortly before use.

Determination procedure: The neutral solution of perrhenate which should contain 0.1 g. rhenium at most, is diluted with hot water to about 50 ml. and after adding 1 ml. of 2N sulfuric acid, heated to about 80°. The solution is precipitated with a 5% Nitron acetate solution adding the reagent until about 0.3–0.4% free Nitron over the amount necessary for precipitation is present. After cooling to room temperature, the solution is cooled in ice water for 2 hours and well stirred several times to insure a quick and complete precipitation of the crystalline Nitron perrhenate since the solution tends to become supersaturated. It is then filtered through a filter crucible of rather fine porosity dried at 110° and the ice cold filtrate used to wash out the beaker and to transfer the precipitate into the crucible. Precipitate and crucible are, depending on the quantity of precipitate, washed with 10–20 ml. of an ice cold 0.3–0.5% aqueous Nitron acetate solution divided in 3–5 portions and sucked completely dry after each addition. The precipitate is then washed 2–3 times with 2–3 ml. portions of ice cold water saturated with Nitron perrhenate to displace any adhering Nitron, taking care not to whirl the precipitate around. After drying 2–3 hours at 110° the precipitate is weighed.

$F/ReO_4 = 0.4442; \log F = 9.64758 - 10.$
$F/Re = 0.3306; \log F = 9.51930 - 10.$

Larger quantities of precipitate are washed with, first, 1 ml. of ice water to remove the main part of the adhering Nitron acetate and after this washed with the saturated aqueous Nitron perrhenate solution to displace the rest of the Nitron acetate. Larger amounts of Nitron acetate naturally lower the solubility of the Nitron perrhenate in water and thus precipitate some Nitron perrhenate from the wash solution. With small amounts this error is neglected but with larger amounts a positive error arises which is compensated for by washing with ice water.

IV. Phenyl Arsenic Acid

1. *The Determination of Zirconium* (*65*)

Zr.

A. C. Rice, H. C. Foggs and C. James, who first proposed using phenyl arsenic acid, recommend the following method for the determination of zirconium: 25 ml. of a zirconium oxychloride solution is diluted to 200 ml., 10 ml. of 10% phenyl arsenic acid added in the cold and the solution heated to boiling. The solution is allowed to boil 1 minute, filtered while hot and the precipitate washed with 1% hydrochloric acid. The dried precipitate is carefully ignited (with the evolution of arsenic!) and finally heated over the blast lamp until all carbon is burned off. The residue is reduced in a stream of hydrogen and finally ignited once more over the blast lamp. After cooling it is weighed as ZrO_2.

The hydrochloric acid concentration of the zirconium oxychloride does not play a part in the determination since the zirconium phenylarsenate is insoluble even in hydrochloric acid of higher concentration.

In the presence of iron (III) salts, the precipitate and the filter must be digested with hydrochloric acid (1 + 1), the solution diluted to 50 ml., again precipitated with 15 ml. of phenyl arsenic acid solution and then treated as above.

In the presence of large amounts of iron (III) salts, the precipitate and the filter are treated with 15 ml. sulfuric acid (1:1), the solution warmed until all the zirconium is in solution, then 50 ml. of conc. hydrochloric acid added, the solution diluted to 500 ml. and precipitated with 30 ml. of phenyl arsenic acid solution.

In the presence of iron (II), aluminum, the elements of the cerium group, manganese, cobalt, nickel, zinc, beryllium, bismuth and copper, the separation is easily carried out. In the presence of thorium, the procedure used above for large amounts of iron must be followed.

Zirconium is quantitatively precipitated in 10% sulfuric acid solutions (by volume). Higher sulfuric acid concentrations have an unfavorable effect. Zirconium can be separated from phosphoric acid by double precipitation in sulfuric acid solution.

Successful separation from uranium is possible in sulfuric acid solutions using the same procedure as for the presence of iron.

1a. Determination of zirconium in iron and steel (*66*)*:* The following method has been used advantageously for this purpose: 5 g. of the sample are dissolved in 50–100 ml. of hydrochloric acid (1 + 1) and oxidized with nitric acid. After cooling, the solution is shaken out with ether, and the ether left removed by heating. Then the solution is diluted to 500 ml. and 50 ml. conc. hydrochloric acid added. After the addition of 50 ml. of 3% hydrogen peroxide, the solution is precipitated with 10 ml. of 2.5% phenyl arsenic acid solution and then heated to boiling temperature for some time. The quick settling precipitate is filtered, washed with 1% hydrochloric acid and ignited (*in a hood with a good draft* (arsenic!)). To remove any silicic acid present, the precipitate is transferred into a platinum crucible taking care not to lose any, 1 ml. of hydrofluoric acid and 2 drops of sulfuric acid added and the crucible heated carefully until the white fumes stop coming off. The residue is ignited and weighed as ZrO_2.

If a precipitate is formed while dissolving the sample in hydrochloric acid, then the solution is concentrated and filtered. The precipitate is fused first with sodium carbonate and then with potassium pyrosulfate. The zirconium thus obtained is precipitated in 10% hydrochloric acid as above and combined with the main precipitate.

2. The Determination of Thorium (65)

Since thorium phenylarsenate is insoluble in solutions which contain considerable acetic acid and the phenylarsenates of the other rare earths are not, the reagent can be used to determine thorium. A. C. Rice, H. C. Foggs, and C. James (65) recommend the following procedure: 25 ml. of a thorium chloride solution are diluted to 500 ml., the solution heated until it begins to boil and then 30 ml. of 10% phenyl arsenic acid, 75 ml. glacial acetic acid and 5 ml. of a saturated ammonium acetate solution added. The precipitate is filtered, washed and then dissolved in 10 ml. of hydrochloric acid. This solution is diluted to 400 ml., heated to boiling and precipitated with 5 g. of oxalic acid. After standing overnight, the thorium oxalate is filtered off, washed, ignited and weighed as ThO_2.

The precipitation of thorium as the oxalate is necessary because thorium phenylarsenate does not give off all its arsenic during the ignition. In the presence of the rare earths the precipitation with phenyl arsenic acid must be repeated.

3. The determination of tin, according to J. S. Knapper, K. A. Craig, and G. C. Chandler (67), can also be carried out by means of phenyl arsenic acid. However, since the method prescribes first changing the tin into metastannic acid, it can scarcely be of great importance. Thus reference to the publication is sufficient.

B. INNER COMPLEX SALTS AS DETERMINATION FORMS

I. Dimethylglyoxime

1. Colorimetric Determination of Small Amounts of Nickel

The determination depends on the fact mentioned by F. Feigl (68) that nickel dimethylglyoxime, on oxidation with PbO_2, gives an intensive red color in alkaline medium forming a four valent nickel compound. M. A. P. Rollet (69) has worked out this method:

Bromine water is added to the nickel solution, which is free from cobalt and copper, until a slight excess of free bromine is present. A little ammonia is now added to remove the excess of bromine and then several drops of an alcoholic dimethylglyoxime solution are added. After 1–2 minutes the red color appears. In a layer about 1 cm. thick, 0.0005 mg. of nickel in 1 ml. can easily be detected. In a larger volume of liquid, even more can be detected.

By using a colorimeter, the determination can be carried out with a relative error of less than 5% with amounts of nickel between 0.001–0.01 mg. per ml. if the unknown and standard solutions are prepared as near as possible at the same time.*

Another use which may be mentioned is the examination of cobalt salts.

In this determination, it is advantageous to change the cobalt into a complex salt, e.g. sodium cobaltic cyanide. By comparison with a sample not treated with dimethylglyoxime, 0.01 mg. of nickel in presence of 1 g. of cobalt can easily be determined.

In determinations with the colorimeter, the yellow color of the sodium cobaltic cyanide is disturbing when the amount of nickel is less than 1 mg. Ni (1 g. Co). In this case a yellow filter is used. For this purpose a layer of concentrated sodium cobaltic cyanide several mms. thick can be used.

By using a spectral photometer the error can be lowered to less than 2%; the absorption is measured at a wave length of approximately 0.55μ.

The method also gives good service in the analysis of nickel steels. As is well known, the precipitate of ferric hydroxide retains nickel. Therefore it is important to take care that the nickel compound is formed at the same moment as the iron precipitate. For this, the dimethylglyoxime must be added before the ammonia. In this way one is sure to find all the nickel in the filtrate of the iron. In chromnickel steels containing 15% Cr and 1% Ni, satisfactory results are obtained.

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* **The unknown and standard solutions should not be more than one hour old at the most.**

The method is suitable to detect nickel in biological material, e.g. ashes of organs.

In order to detect or to determine quantitatively (colorimetry) very small amounts of nickel in the presence of much larger amounts of other cations (e.g. zinc), a method common in England (70) is used in the following way.* The acid reacting solution (of the preparation) is evaporated almost to dryness on the hot plate and after cooling, the residue is diluted to a suitable volume (200 ml.). Sufficient NH_4Cl (20 g.) is added and then HCl added until the solution reacts acid to litmus (but not to congo red). Then 0.1 g. tartaric acid, 1 ml. of 10% sodium-hypochlorite solution and 5 ml. of ammonia (Sp. Gr. = 0.880) is added to the cold solution. Then 1 ml. of a 1% alcoholic solution of dimethylglyoxime is added to the solution which is now alkaline to litmus and the solution again diluted (to 300 ml.). After waiting 2 minutes the color is compared with a solution of known nickel content (also containing the other salts present in the unknown, e.g. $ZnCl_2$). A photoelectric cell is excellent for this purpose; compare with (70).

2. Determination of Palladium; Its Separation from Copper and Iron

M. Wunder and V. Thüringer (71) found that palladium forms a yellow complex salt analogous in composition to nickel dimethylglyoxime—as proven by a content of 31.61% Pd. The precipitation succeeds best in a hydrochloric acid dimethylglyoxime solution and is carried out as follows: The acid palladium salt solution is diluted to 150 ml. with water and the necessary amount of a 1% hydrochloric acid dimethylglyoxime solution added to it; that is, for 1 part of Pd, 3 parts of reagent. The solution is now heated ½ hour on the water bath until the yellow precipitate has settled and filtered while still warm. The precipitate is washed with warm, dilute hydrochloric acid, dried and ignited. The ignition must be done very carefully, especially watching that no vigorous evolution of fumes occurs which might carry off large amounts of metal. A very small flame is used until the filter is charred and at the end the ignition is finished over the blast lamp.

For the separation of palladium from iron and copper, the authors recommend the following procedure: A sufficient quantity of dimethylglyoxime (hydrochloric acid solution) is added to the solution which contains the three metals; if iron is in the trivalent form a large excess of reagent must be added since it is needed by the iron (reduction of Fe(III) → Fe(II) salts). After all the iron is reduced the palladium compound begins to come down. The reaction is accelerated by careful heating. The precipitate obtained is treated as announced above. Iron and copper in the filtrate are separated, or determined by one of the usual methods.

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* From a personal communication of Dr. W. Boettger, Hannover.

3. Separation of Nickel from Palladium (72)

A 1% solution of dimethylglyoxime in 2% hydrochloric acid is added to the weakly acidified (HCl) solution of both metals, the solution allowed to stand for ½ hour on the water bath and the yellow palladium precipitate filtered out while the solution is still warm. The precipitate is washed with boiling water, dried, ignited and the metallic palladium left is weighed. The filtrate, which contains all of the nickel, is heated to boiling, made weakly alkaline with ammonia and the precipitated nickel dimethylglyoxime filtered as usual through a dried filter crucible.

According to M. Wunder and V. Thüringer (73), dimethylglyoxime can be used to separate gold from palladium, platinum from palladium and palladium from rhodium. The methods for these separations are described in the original publication.

II. Quinaldinic Acid

Preparation of reagent (16): A solution of 48 g. bromine in 100 g. glacial acetic acid are added dropwise to a mixture of 14 g. quinaldine, 50 g. of water free anhydrous sodium acetate and 100 g. of glacial acid. After all the bromine is put in, the solution is heated for a short time. The tri-bromide formed is recrystallized from glacial acetic acid or alcohol. M.P. = 56°. The hydrolyzation of the bromide to quinaldinic acid is accomplished by boiling with dilute (1 + 1) sulphuric acid. The acid is purified over copper salt obtained through the dropwise addition of an aqueous solution of the acid to a boiling acidified copper sulphate solution. The copper sulphate is decomposed by hydrogen sulphide and the quinaldinic acid recrystallized from glacial acetic acid. M.P. = 155–156°. A 3.3% solution of the free acid or the corresponding amount of the sodium salt is used as reagent.

α. INDIVIDUAL DETERMINATIONS

1. Copper (16) Cu.

Since copper quinaldinate is insoluble in dilute sulphuric acid and in dilute acetic acid, the quantitative determination of copper can be carried out in sulphuric acid as well as acetic acid solution. The salt precipitated in the hot and dried at 125° has the composition $(C_{10}H_6NO_2)_2Cu \cdot H_2O$, corresponding to a copper content of 14.96% Cu.

Determination procedure: The aqueous solution of the copper salt which should be 150 to 160 ml. for about 0.1 g. Cu is acidified with 2–5 ml. 2N sulphuric acid and heated to boiling. A solution of the sodium salt of the quinaldinic acid (5.636 g. Na-salt, corresponding to 5 g. acid, in a 150 ml. water) is added dropwise with stirring until in slight excess. The green crystalline precipitate which forms immediately settles out after several minutes. The precipitate is washed by decanting with hot water, transferred into a filter crucible and again washed with hot water until all traces of the reagent are removed. The precipitate is dried at 125° to constant weight. $F = 0.1496$; $\log F = 9.17486-10$. Time of determination: about one to two hours. Results: excellent.

The method of A. M. Sanko and G. A. Butenko (74) can be advantageously used to determine copper in cast iron and steel. The authors recommend the following procedure:

1 g. of material is dissolved in 15–20 ml. of hydrochloric acid (1 + 1) and after adding 2–3 ml. of nitric acid (Sp. Gr. = 1.4) to oxidize the iron, the solution is boiled until no more NO_2 fumes are given off. The solution is washed into a porcelain dish, evaporated to dryness and the silicic acid filtered off as usual. The impure silicic acid is now ignited, the silica removed by the usual treatment with hydrofluoric and sulfuric acid and the residue dissolved in water and combined with the silicic acid filtrate. 6 g. of tartaric acid are added to the filtrate, the solution neutralized with ammonia, 15 ml. of 4N sulfuric acid are added and the copper precipitated by the dropwise addition of an excess of sodium quinaldinate. After standing 18 hours, the precipitate is filtered through a filter crucible, washed with hot water and dried at 125°.

1a. Micro determination (75): The micro determination is carried out either in a micro beaker or in a porcelain crucible together with a weighed filter stick. All the essentials relative to the pipetting in of a solution were described on page 41. If a solid salt is to be analyzed it is weighed directly in the micro beaker and then dissolved in a little water. (1–2 ml. for 1 mg. Cu.; the determination of larger amounts is unsatisfactory because then it is difficult to carry out the filtration.)

Determination procedure: The copper salt weighed into a micro beaker dried at 125° is dissolved in 1–2 ml. of water and the solution acidified with 1 drop (0.025 ml.) of 0.7N sulphuric acid. The filter beaker is placed on a boiling water bath and the reagent solution (1% solution of recrystallized quinaldinic acid in water) is added dropwise to the hot solution. After each addition of a drop the beaker is shaken gently and the next drop of the reagent is not added until the precipitate formed has settled. When all the copper is precipitated 4 drops more (about 0.1 ml.) of the reagent in excess is added. (The amount of the aqueous solution of quinaldinic acid added in excess is independent of copper present.) After precipitation is complete the beaker is placed on a water bath for 5-10 minutes. After this the supernatant liquid is filtered off and the precipitate washed by decanting with hot water 6 times. During the filtering and washing the beaker is kept on the water bath. In order to simplify the filtration care should be taken that no part of the precipitate remains on the filter stick before the washing is finished. Otherwise the precipitate would plug up the filter stick and thus the filtration would be very much retarded. When the washing is finished, the beaker and the filter stick are dried 10–12 minutes at 125° in a hot air stream. After the usual cleaning, the beaker and the filter stick are weighed on the micro balance.

The check analyses announced by the authors do not show such good agreement as the macro determinations. However, the exactness appears, despite this, to still be sufficient.

2. Cadmium (16) Cd.

The cadmium salt of the quinaldinic acid can be quantitatively precipitated from an acetic acid or from a neutral solution. In contrast to the copper salt, the cadmium salt dried at 125° is free from water of crystallization corresponding to the formula $(C_{10}H_6NO_2)_2Cd$ with a cadmium content of 24.62%.

Determination procedure: The solution made up to 150 ml. for 0.1–0.2 g. of cadmium is warmed several minutes on the water bath and the reagent solution added dropwise under strong stirring until precipitation is complete. Now it is just neutralized with dilute sodium hydroxide and the white, granular precipitate allowed to settle out. After cooling to room temperature, the precipitate is decanted with cold water, filtered in a filter crucible and washed with cold water until the complete removal of the reagent excess. After drying for a short time at 125°, constant weight is reached. $F = 0.2462$; $\log F = 9.39123-10$. Time of determination about 1½ hours. Results—excellent.

3. Zinc (*16*)

The zinc salt dried at 125° has the formula $(C_{10}H_6NO_2)_2Zn \cdot H_2O$.

Determination procedure: 2–5 ml. of dilute acetic acid are added to the solution which should be made up to about 150 ml. for 0.1 g. Zn and the solution heated to boiling; then reagent solution is added dropwise with stirring until all of the zinc is precipitated. The precipitate comes down after several minutes and is, as announced under copper, decanted with hot water, washed and finally dried at 125° to constant weight. Time of the determination: about 1½ hours. The check analyses done show excellent agreement with the values of the standard solution.

$F = 0.15295$; $\log F = 9.18454{-}10$.

3a. Micro determination (*75*)*:* The weighed zinc salt corresponding to approximately 1 mg. Zn is dissolved in a micro beaker in 1–1.5 ml. of water, the solution acidified by the addition of 1–2 micro drops (0.02–0.04 ml.) of glacial acetic acid and then placed on a boiling water bath for a minute. Precipitation is accomplished by the dropwise addition of a sodium quinaldinate solution (corresponding to 1 g. quinaldinic acid in 100 ml.) shaking steadily during the precipitation. After completion of the precipitation, an excess of 0.2–0.25 ml. over the theoretical amount is added. (For 1 ml. of precipitant used, 0.2 ml. of excess is added.) Finally the micro beaker is heated on the water bath for several minutes and the precipitate allowed to come down. The supernatant liquid is now sucked through the filter stick and the precipitate sucked as nearly dry as possible. The precipitate is washed 5–6 times with 0.5–1 ml. of hot water, the beaker and filter stick placed on the boiling water bath in order to remove the clinging drops and finally dried at 125° in an air stream to constant weight.

4. Uranium (*16*) U4.

Uranium forms basic salts with quinaldinic acid which are well suited to precipitate small amounts of uranium. Concerning the composition of the precipitates, nothing is known.

Determination procedure: 5–7 g. ammonium chloride is added to the solution of the uranyl nitrate, the solution diluted to 120 ml. and heated to boiling. The reagent is added dropwise in excess to the hot solution with stirring and the precipitate transferred to a filter and washed with a hot solution containing 5% hexamethylenetetramine and 5% ammonium nitrate until the chloride test is negative. The precipitate is placed wet in a platinum crucible, ignited and weighed as U_3O_8.

β. SEPARATIONS

1. Separation of Copper from Cadmium (16)

The copper in the boiling hot solution which contains both metals and which should be made up to about 150 to 160 ml., is precipitated after acidifying with 2N sulfuric acid exactly as was announced for the determination of copper. Filtrate and wash water from the copper precipitation are evaporated to about 160 ml. and neutralized with ammonia under stirring. As a result, the greatest part of the cadmium precipitates out. To complete the precipitation more reagent is added as the sodium salt. In general the procedure already announced for the determination of cadmium is followed.

2. Separation of Copper from Lead (16)

7 to 15 ml. of glacial acetic acid are added to the solution made up to about 200 ml. and the solution heated. The sodium quinaldinate solution is added in dropwise to this hot solution with stirring until precipitation is complete, then 1 ml. more reagent solution is added. The clear liquid is filtered through a filter crucible and washed with a solution containing 1 ml. of glacial acetic acid and 3 to 5 drops of sodium quinaldinate solution for 50 ml. of water. Finally the precipitate is washed several times more with hot water and dried at 125° to constant weight. The lead in the filtrate is determined after one of the usual methods, preferably as the sulfate by fuming with sulfuric acid.

3. Separation of Copper from Manganese, Nickel and Cobalt (16)

5–8 ml. of 2N sulfuric acid are added to the solution made up to 200 ml. and the copper, as already described, precipitated with quinaldinic acid. As wash solution, hot water containing 2.5 ml. of 2N sulfuric acid and 1 ml. of reagent solution (sodium salt) to 100 ml. water is used. Finally the precipitate is washed several times more with hot water to remove the last traces of the sodium salt.

4. Determination of Copper in the Presence of Phosphoric Acid, Arsenic Acid and Arsenous Acid (16)

If a solution exists, which contains the mentioned acids besides copper, then the copper is determined in an acetic acid solution (for 200 ml. of solution about 6–10 ml. of glacial acetic are added). As wash solution, acetic acid (1 + 40), to which several drops of reagent solution are added is used. Finally the precipitate is washed with hot water in order to remove the last traces of the wash solution.

1a–4a. Micro analytical procedure of separation (*76*)*:* The micro determination described on page 56 for copper is also adaptable for the micro analytical separation from the above ions if the wash solution mentioned for the individual determinations is used.

5. Separation of Zinc from Manganese (*77*)

The separation is based upon the solubility of manganese quinaldinate in dilute acetic acid.

Separation procedure: 5–10 ml. glacial acetic acid for each 200 ml. are added to the unknown, the solution heated to boiling and the reagent solution added dropwise with stirring to the hot solution until in slight excess. Now the solution is decanted through a filter crucible, the precipitate rinsed into the crucible with dilute hot acetic acid (1:40) and finally washed with hot water.

In the filtrate the manganese is precipitated as the sulfide and determined as $MnSO_4$.

6. Separation of Zinc from Magnesium (*77*)

2 ml. of glacial acetic acid are added to the hot solution of both of the salts diluted to about 200 ml. and the zinc precipitated by the dropwise addition of the reagent solution with stirring. After a short time the precipitate has completely settled and can be brought into a filter crucible where it is washed with hot water. In the filtrate, the magnesium is determined as the pyrophosphate.

7. Separation of Zinc from Calcium and Barium (*77*)

The separation can be carried out in the same way as the separation from magnesium. The zinc is precipitated out of a solution which contains 3–6 ml. of glacial acetic acid for 170 ml. of solution.

8. Separation of Zinc from Phosphoric Acid (*77*)

Sodium carbonate is added to the mineral acid solution until it begins to be turbid then the solution is clarified with about 6 ml. of glacial acetic acid. The solution is now diluted with water to 200 ml. and heated—during which the solution must stay completely clear. The reagent solution is then added dropwise to the hot solution until no more precipitation occurs. The precipitate settles after a few minutes and after transferring to a filter crucible with water which contains several drops of acetic acid and reagent solution, is finally washed with pure water.

5a–8a. Micro analytical procedure for the above separations (78): The procedure used for the micro zinc determination has also proven adaptable for the micro separation if the amount of glacial acetic acid (0.05–0.1 ml.) added is measured according to the quantity of foreign ions. A solution which contains 2.5 ml. glacial acetic acid and 5 ml. of sodium quinaldinate to 100 ml. of solution is used as wash solution. The precipitate is washed three times with this hot solution using a total of 1.5 to 3 ml. To remove the wash solution, the precipitate is washed three times more with hot water.

For the separation of zinc from the alkali earths and from magnesium, it is advantageous to add a smaller amount of glacial acetic acid.

9. Separation of Zinc from Iron, Aluminum, Uranium, Beryllium, Titanium (77)

As mentioned, the metals named form amorphous yellow precipitates with quinaldinic acid in weak acid solution. However, if sufficient tartaric acid is added to a weak mineral acid solution and the solution neutralized with ammonia, then none are precipitated by quinaldinic acid. By utilizing this property zinc can be separated from these metals.

Chromium cannot be separated from zinc in this way, since the filtrate always contains some zinc. (The zinc value is about 2–3% too low.)

Separation procedure: To the solution oxidized for the presence of ferrous salts with several drops of nitric acid and some ammonia, four to five g. of sodium tartrate are added after the cooling and the solution neutralized exactly with ammonia using a mixture of methyl red and methylene blue as indicator. A drop of 2N ammonia is added to the neutral solution, the solution diluted to 150–160 ml. and heated to 50°. A solution of ammonium quinaldinate in slight excess is now added dropwise under constant stirring and the precipitate allowed to settle. (An excess of ammonia is to be carefully avoided, since the zinc quinaldinate is soluble in ammoniacal solution.) After the precipitate has settled, it is filtered through a filter crucible washed with hot water, and dried at 125°.

The ions present in the filtrate after the destruction of the tartaric acid by fuming sulfuric acid are determined as usual. If it is only of concern to separate zinc from iron, then the fuming of the filtrate with sulfuric acid can be omitted by first precipitating the iron as the sulfide, dissolving this precipitate in dilute hydrochloric acid and finally determining as Fe_2O_3.

According to the check analyses announced by the authors, the method gives well agreeing values although somewhat too low results would not be surprising, in view of the slight solubility of the zinc quinaldinate in ammonia.

9a. Micro analytical separation procedure (79): Several drops of bromine water are added to the solution, which contains 0.15–1 mg. Zn in about 1.5 ml., in order to oxidize any divalent iron present. After this 0.4–1 ml. of a 5% sodium tartrate solution are added and gaseous ammonia passed through the solution until the odor of the ammonia just predominates. Thus the solution is very weakly ammoniacal. (Perhaps it is also recommendable here to prove this relation with the above indicator.) To the solution so prepared, a solution of sodium quinaldinate (corresponding to 1 g. quinaldinic acid in 100 ml.) is added dropwise with occasional shaking of the micro beaker. After the theoretical amount of solution (0.2–1 ml.) is added a drop at a time, 0.2–0.25 ml. more in excess is added, the beaker put on a water bath and the excess of ammonia removed by passing an air stream not above a temperature of 60° through the solution. When the ammonia excess is completely removed, the beaker is quickly cooled and the zinc quinaldinate is filtered through a micro filter stick, washed with hot water and dried in an air stream at 125°. Results are satisfactory.

In the presence of iron care must be taken that no reduction of it occurs since otherwise the red ferrous salt immediately arises and is coprecipitated with the zinc salt, giving a red violet color to the latter. By careful work (replacing the ammonia with air at a temperature not above 50–60° at the highest, quickly cooling and filtering) it is possible however, to obtain a completely white zinc salt in the presence of iron. The presence of Al, U, Be and Ti offer no difficulty for the determination of zinc.

10. Colorimetric Determination of Iron (16)

The reaction of quinaldinic acid with ferrous salts already mentioned earlier can be used for the colorimetric determination of divalent iron. Sodium quinaldinate gives a pale red color with very dilute, neutral ferrous salt solutions—with concentrated solutions, a dark red color. By adding dilute potassium cyanide solution the color is intensified.

Any ferric iron present is reduced by adding hydroxylamine hydrochloride. The method allows iron to be determined in the presence of rather moderately large amounts of Cu, Ni, Co and Zn. Very large amounts of aluminum and copper complicate the quantitative determination on account of the insolubility of their precipitates or through blocking of the color of the iron complex.

Determination procedure: To the solution to be tested, 1 ml. of a 5% hydroxylamine hydrochloride solution and 1 ml. of 10% potassium cyanide solution are added in that order and then the solution diluted to 100 ml. with water. During measurement in the colorimeter the solution must be cooled and the standard solution also treated in the same way since the pale red color soon fades on standing, especially at higher temperatures. In this way, values are obtained which are in excellent agreement with the gravimetric results.

Concentration limit: 1:14,500,000.

Limit of identification: 0.172γ.

In the presence of 1000 parts of copper to 1 part of iron, the concentration limit is only 1:6,000,000, in the presence of 2000 parts the limit of identification is not more than 1.72γ.

This same identification limit is reached in the presence of 800 parts of cobalt or nickel.

Recovery of the reagent: It is best if the filtrate and precipitate are treated separately. The copper salt is precipitated out of the filtrate with H_2S, the copper sulfide filtered out, the filtrate evaporated and the acid recrystallized out of glacial acetic acid.

The copper and cadmium compounds are decomposed by hydrogen sulfide and the acid purified by evaporation and recrystallization out of glacial acetic acid.

The zinc salt is dissolved in hydrochloric acid, the solution diluted until a precipitate just comes out and then copper sulfate solution added. The copper salt is decomposed as announced above.

III. Benzoin Oxime, "Cupron" (17)

The reagent in ammoniacal solution forms an easily filterable, heavy precipitate with copper which is insoluble in water, alcohol, dilute ammonia, acetic acid and tartaric acid. In concentrated ammonia it is somewhat soluble and easily soluble in mineral acids.

Since the precipitation is also quantitative in ammoniacal tartrate solution, benzoin oxime can be used to separate copper from iron, lead and all the metals whose hydroxides are not precipitated in solutions containing tartrate.

The separation of copper from cadmium, zinc, cobalt and nickel is made possible by the fact that these metals do not form insoluble precipitates with benzoin oxime in ammoniacal solution. Unfortunately, the separation of copper from nickel cannot be satisfactorily carried out in this way since the latter is always in part coprecipitated with the copper in weakly ammoniacal solution, and as a result errors up to 2% are obtained. However, a satisfactorily exact separation can be accomplished by precipitating in tartaric acid solution buffered with tartrate.

1. Determination Procedure (17)

To the solution to be tested, which should be neutral and as free as possible from ammonia salts, dilute ammonia is added until a clear blue solution appears. The solution is now heated to boiling and precipitated by the dropwise addition of an alcoholic solution of the reagent. The precipitation is finished when the blue color of the cupriamine salt disappears. The dark green, heavy precipitate is collected in a filter crucible and first washed with hot, diluted ammonia (one part concentrated ammonia to 100 parts of water) and after this with hot water. Since the precipitate is amorphous, the last remainder of the precipitant cannot be removed in this way. This is accomplished by drying the above precipitate first at 105–115°, then washing with warm alcohol and finally with water. The precipitate dried at 105–115° to constant weight is free from excess of reagent.

$F = 0.2202$; $\log F = 9.34282 - 10$.

Limit of identification: 0.1γ copper.

Concentration limit: 1:500,000.

1a. Separation of copper from nickel: The copper is precipitated out of a tartaric acid solution which was buffered by the addition of sodium potassium tartrate.

1b. Separation of copper from lead, aluminum, iron, etc.: Sodium potassium tartrate or sodium tartrate is added in sufficient quantity to the solution to prevent the precipitation of the corresponding hydroxides before adding the ammonia.

1c. The determination of copper in steel (80): H. A. Kar (80) carried out the determination of copper in steels alloyed with copper and molybdenum.

Determination procedure: 2–5 g. of the alloy, depending on the copper content, are placed in a 600 ml. beaker, 50–100 ml. of 10% sulfuric acid poured over it and heated until the reaction is finished. In the absence of vanadium, the solution is diluted to 250 ml. with hot water and heated to boiling. Now 1 g. of sodium thiosulfate dissolved in 10–50 ml. of water is added for each gram of steel, the boiling continued for 10–15 minutes and the precipitate allowed to settle.

If vanadium is present, several crystals of potassium chlorate are added to the sulfuric acid solution and the solution heated until they are dissolved. Then the solution is diluted to 400 ml. with hot water, saturated with hydrogen sulfide for about 15 minutes and the precipitate allowed to settle. The precipitate is filtered through a thick filter under weak suction and the filter and the beaker washed several times with 1% sulfuric acid. The precipitate and the filter are ignited in a quartz crucible, cooled by pouring 10 ml. of hydrochloric acid over the precipitate, and then heated until the residue goes into solution. This solution is transferred to a 400 ml. beaker, 2–3 drops of nitric acid added and then an excess of ammonia. The solution is heated to boiling, filtered into a 600 ml. beaker and the filter washed several times with hot, ammoniacal water. The filtrate is diluted with 250 ml. of hot water, heated to boiling and precipitated by slowly adding 10–15 ml. of reagent solution with steady stirring. The solution is boiled 1 minute, some filter pulp added (Schleicher and Schull, # 292) and filtered through a black band filter. The precipitate is washed 5–6 times with hot, 3% ammonia, the filter and the precipitate burned in a quartz crucible and weighed as CuO.

Tungsten steels are treated in the following way:

2–5 g. are heated in a 600 ml. beaker with 50 ml. of conc. hydrochloric acid until the reaction is complete, 5 ml. of nitric acid added and the solution evaporated to dryness. 25 ml. of hydrochloric acid are poured over the cooled residue and the solution heated in order to dissolve the iron, chromium, etc. After adding several crystals of potassium chlorate, the solution is heated strongly until all the tungstic acid is precipitated. After the precipitate has settled, it is filtered and washed about 10 times with cold 5% hydrochloric acid. 10–25 g. of citric acid are added to the filtrate and then it is made alkaline with ammonia. It is now acidified with hydrochloric acid adding a 2 ml. excess for each 100 ml. of solution. The boiling hot solution is then saturated with hydrogen sulfide, the precipitate filtered off, and then the above procedure followed.

2. Micro Determination

A recheck of the precipitation procedure worked out by R. Strebinger (81), by F. Hecht and R. Reissner (82), has proven this method somewhat inaccurate. The last named authors recommend a precipitation procedure analogous to the macro method which gives usable results—as shown by the check analyses obtained.

Determination procedure: The copper nitrate solution acidified with nitric acid is evaporated to dryness in a weighed porcelain crucible together with the filter stick to remove large amounts of acid, the residue dissolved with three drops of 6.5% nitric acid and 2 ml. of water and cold 10% ammonia is added to it until a blue colored, clear solution is obtained. Then 1 ml. of a 1% alcoholic benzoin oxime solution for 0.5–0.6 mg. CuO is allowed to drop in from a micro pipette with steady shaking. Now the solution is heated for ten minutes on a gently boiling water bath which suffices to completely clarify the supernatant liquid. The alcohol evaporated during the heating is replaced from time to time. This is necessary in order to avoid the formation of a crust on the wall of the crucible which cannot be completely washed off with alcohol afterwards.

The hot solution is now filtered through a "Tauch" filter and washed twice with 1 ml. portions of hot 1% ammonia, twice with hot water and once with hot alcohol. The precipitate is dried at 105–110° more advantageously by sucking dust free air through it. The precipitate thus dried is covered over with 1–2 ml. hot 96% alcohol and crushed as fine as possible with the Tauch filter. After this, the solution is warmed for five minutes on the gently boiling water bath and filtered while still warm. Finally the precipitate is washed once more with hot water and dried at 105-110° to constant weight.

The use of the filter beaker for the determination is not recommended because then it is impossible to finely crush the precipitate after the first drying, as is possible with the Tauch filter. A bare shaking with hot alcohol is, because of the condition of the precipitate, not sufficient to completely free it from the excess of reagent.

3. The Determination of Molybdenum (83)

H. B. Knowles (83) recommends the following procedure:

The solution to be examined which contains 10 ml. of conc. sulfuric acid and at most 0.15 g. of molybdenum in 200 ml. of solution is, in the presence of vanadate or chromate, reduced in the usual manner with sulfurous acid. The excess sulfur dioxide is boiled off, the solution cooled to 5–10° and 15 ml. of a solution of 2 g. benzoin oxime in 100 ml. alcohol added to it for each 0.1 g. Mo. Now bromine water is added until the solution is slightly yellow and then several millimeters more of the reagent. After 10–15 minutes standing, some filter pulp (Schleicher and Schull, #292) is added and the solution filtered. A freshly prepared solution containing 25–50 ml. of reagent solution and 10 ml. of sulfuric acid in a liter of water is used to wash the precipitate. After the precipitate has been thoroughly washed (about 200 ml. is necessary) it is transferred to a platinum crucible and carefully ignited to MoO_3. If sufficient reagent was added, needle shaped crystals of benzoin oxime precipitate out in the filtrate on standing.

If tungsten, palladium, chromate, vanadate, tantalum, niobium or silicic acid are present, they must be removed before the molybdenum precipitation.

The method is suitable for determining molybdenum in molybdenum steels and molybdenum alloys.

IV. Salicylaldoxime (18)

Preparation of the reagent: 1 g. of salicylaldoxime is dissolved in 5 ml. of alcohol without warming and this solution slowly poured into 95 ml. of water at 80°. Thereby the oxime partially separates out in the form of a fine oil suspension, but the oil droplets quickly again dissolve. Shaking is to be avoided, since this again unites the droplets. After the solution has become clear, one shakes for a short time and filters.

According to S. Astin and H. L. Riley (84), it is not necessary to start with the commercial product. A usable reagent solution is obtained by the following procedure: 2.22 g. of salicylaldehyde dissolved in 8 ml. of alcohol are added to a solution of 1.27 g. of hydroxylamine hydrochloride in 2 ml. of water, diluted with 15 ml. of alcohol and the mixture slowly poured into 225 ml. of water at 80° under constant stirring. This solution contains very nearly 1% of the reagent.

INDIVIDUAL DETERMINATIONS

1. Copper

Determination procedure: To the solution to be tested, whose volume should be within the optimal analytical concentration, 2N sodium hydroxide is added until a lasting precipitate is formed. This is then brought into solution by the addition of several drops of acetic acid. Now the solution is precipitated at room temperature with salicylaldoxime, using it in as small an excess as possible. The precipitate comes down immediately and coagulates easily on stirring. The clear supernatant liquid is tested for completeness of precipitation by adding several drops of reagent. A considerable excess of the reagent does not, however, influence the results, but it is to be avoided, since then the washing must be continued for a long time. It is essential that the last traces of oxime be removed from the precipitate, otherwise the precipitate is visibly decomposed during drying. The precipitate is filtered through a porcelain filter crucible and washed with cold water until the filtrate no longer gives any color with ferrous chloride. During the washing, care is taken that the precipitate always remains moist. Finally the precipitate is washed twice more with cold water and then sucked to complete dryness. The precipitate, dried as much as possible by suction, is dried at 105–110°. Constant weight is usually reached after one hour. Drying at a higher temperature (over 115°) causes a slight loss in weight.

F = 0.1895; log F = 9.27761–10.

Limit of identification: 0.5γ Cu.

Concentration limit: 1:100,000.

1a. Micro determination: F. Hecht and R. Reissner (82) give the following precipitation procedure: The solution is evaporated to dryness to remove larger amounts of acid, the residue dissolved with 3 drops (1 drop = 0.025 ml.) of 6.5% nitric acid and the solution sucked over into a filter beaker. The volume so obtained may contain as much as 3 ml. 1 to 2% sodium hydroxide is now added in the cold until a lasting turbidity occurs and then dilute (1:4) acetic acid added until this turbidity just vanishes. Now a small excess of the reagent is added to the cold solution and the precipitate shaken so it will clump together. After allowing to settle 5 to 10 minutes, it is filtered. The precipitate is washed with cold water until the filtrate no longer gives a violet color when tested with ferric chloride (2 to 3 washings are necessary) and dried at 100–105°.

1b. Nephelometric determination of copper: H. Alten, H. Wandrowsky and E. Knippenberg (85) recommend the following procedure for the nephelometric determination of copper in lead free substances: The unknown and the standard solutions exactly neutralized with ammonia are poured into graduated glass cylinders of 25 ml. capacity (30–100γ Cu) or of 15 ml. capacity (10–30γ Cu), then 3 ml. 30% acetic acid, 1 ml. 20% potassium citrate, 2 ml. of a saturated solution of mono-potassium phosphate (after Sørensen) and 0.5 ml. of saturated sodium acetate solution are added to each cylinder, the mixture diluted to the 22 ml. or 12 ml. mark—depending on the cylinder, and then mixed with a glass rod. The reagent cylinder is placed in a container with water to keep the temperature constant. Then 1 ml. of reagent solution is added and the solution stirred. After standing 1½ hours (30–100γ Cu) or 2½ hours (10–30γ Cu), 1 ml. of acetic acid is added and mixed, and after standing 30 minutes more, the relative turbidity is determined. The reagent cylinder is kept in water all the time in order to prevent a change in temperature. The turbidity measurement is done in a "Stufenphotometer" with the brightness set at 4 and with a red filter of the special glass recommended by Zangemeister. 3 parallel determinations are carried out and also a blank determination on the reagents used.

Exact measurement of the reagents and constant temperature of the solution is necessary for the determination since the turbidity value increases with rising temperature. The determination is disturbed by iron salts. The influence of the iron salts can be somewhat reduced through the addition of potassium phosphate and potassium citrate and through an increase in the acidity of the solution. The influence of the iron can be completely eliminated by adding an iron salt to the standard solution until the color tone of the solutions is about the same. It is not necessary that the concentration of the iron in the unknown and the standard solutions be the same.

As a result of thorough investigations it has been shown that the specificity of the salicylaldoxime does not hold as closely as was first announced; many divalent metals, for example, form such strong complexes with the reagent that no hydroxides are precipitated with sodium hydroxide. It was found that the solubility of these complexes in acetic acid increases in the following order: Cu, Ni, Co, Zn, Cd, Ag, Pb, Hg(II). Palladium occupies a special position in so far as it can be quantitatively precipitated from a weak mineral acid solution. However, in dilute acetic acid, ammonia salt solutions, sodium hydroxide and 96% alcohol the compound is soluble. The lead salicylaldoxime on the other hand is quantitatively precipitated out of an ammoniacal solution.

2. Determination of Palladium; Its Separation from Platinum

H. Holzer (86) gives the following directions for carrying out this determination microanalytically: A filtered, hot-saturated, aqueous solution of salicylaldoxime is added to a weak mineral acid palladium solution in a micro beaker. The egg yellow coloring formed is coagulated and precipitated by careful shaking. After half an hour standing, the precipitate is siphoned into a Neubauer micro crucible, the filter apparatus rinsed alternatingly with cold water and 30% alcohol in order to bring the last traces of the precipitate into the crucible, and then the precipitate washed with cold water and 30% alcohol several times. The precipitate is dried at 110° to constant weight.

The check analyses for the individual determinations as well as for the separation of the palladium from platinum showed satisfactory values.

$F = 0.2817$; $\log F = 9.44979-10$.

3. Separation of Copper from Iron

According to the announcement of Ephraim (20), it is better in this case to work in very weak hydrochloric acid solution since the copper precipitated out of an acetic acid solution always contains iron.

Separation procedure: To the mineral acid solution, which contains copper and iron, sodium carbonate is added dropwise until stirring redissolves the precipitate but forms a deep brown colloidal solution. This procedure is similar to the well known acetate separation of Brunck. The copper can now be precipitated from this solution by adding salicylaldoxime in the cold. The iron in the deep, dark colored filtrate can be precipitated as the hydroxide after destruction of the excess reagent. For this purpose, one adds bromine water gradually to the filtrate until it becomes lighter. Thereby the oxime is destroyed and a precipitate of organic acid is formed. By adding ammonia the acid dissolves very easily, while at the same time the iron hydroxide precipitates. After some digestion the iron hydroxide is filtered off, washed with hot water and determined as Fe_2O_3.

A yellow coloring of the filtrate is not caused by the iron but by traces of organic substance which also stubbornly cling to the iron hydroxide. It is, however, unnecessary to wash the precipitate until the filtrate is completely colorless since the organic matter is completely destroyed in the following ignition.

I. Ubaldini (87) applies this method to a rapid determination of copper in pyrites. The determination is carried out as follows: Aqua regia is added to 1 g. of the finely pulverized pyrites and the solution then evaporated to dryness on the water bath. The residue is taken up with conc. hydrochloric acid, diluted with water, filtered and washed with water until the iron reaction disappears. 5 g. of tartaric acid are added to the filtrate, the filtrate made weakly alkaline with ammonia and then acidified with dilute acetic acid. The copper is precipitated from this solution with 5 ml. of the reagent solution. The precipitate is filtered through a filter crucible and dried as usual.

4. Separation of Copper from Nickel (88)

1 g. of crystallized sodium acetate and 10 ml. of glacial acetic acid are added to the solution which contains copper and nickel and the solution diluted to 100 ml. with water. Now an excess of 1% reagent solution sufficient to precipitate both metals is added. The solution is vigorously stirred to coagulate the precipitate and allowed to stand over night. The precipitate is now filtered through a coarse fritted glass crucible, washed with cold water, dried at 100° and weighed.

The filtrate (300-350 ml.) which contains all the nickel is almost neutralized with ammonia—thus making the solution just slightly acid. By stirring, the luminous green precipitate is easily coagulated, then filtered through a filter crucible and the precipitate washed with cold water until the filtrate no longer gives a reaction with ferric chloride.

The check results published by the authors (84, 88) show that the separation gives good results even in a copper-nickel ratio of 5:1.

Finally there is still a paper of Ishibashi and Kishi (89) to be mentioned. They precipitate lead quantitatively from an ammoniacal solution by means of salicylaldoxime. A small excess of reagent is added to the lead solution, the solution made alkaline with dilute ammonia, and filtered. The easily filterable precipitate is washed with alcohol, dried at 105° and weighed.

V. Oxalene-diuramino-oxime

According to F. Feigl and A. Christiani-Kronwald (22), the water soluble reagent is suitable for the determination of nickel and its separation from cobalt.

Preparation of the reagent: The parent material for this compound is obtained according to the method of E. Fischer (90) by passing cyanide gas into a cooled, alkaline solution of hydroxylamine hydrochloride, and the product purified by recrystallization out of the water. The reagent is prepared by the method of W. Zinkeisen (91): One mol of the pure product is dissolved in water, 2 mols of hydrochloric acid (d = 1.19) added to it and then an aqueous solution of 2 mols of potassium cyanide poured in. A white crystalline mass of oxalene-diuramino-oxime immediately precipitates out, which, after the recrystallization out of hot water, has a melting point of 191°. The yield is about 80% of the theoretical.

The reagent forms an orange colored precipitate with nickel salts in aqueous ammoniacal solution having the composition of an ammoniakate, Ni ($C_4H_{12}O_4N_8$), which is completely insoluble in water and ammonia at room temperature. At boiling temperature, however, it is noticeably soluble.

Determination procedure: The nickel solution to be analyzed is made ammoniacal and an excess of the reagent added to it with stirring. The solution is now warmed one to two minutes to boiling and then allowed to stand five hours in the cold, whereby the finely crystalline precipitate settles out and the solution becomes colorless. The precipitate is collected on a filter, washed several times with cold water and dried to constant weight at 110–113°.

$F = 0.1992$; $\log F = 9.29929-10$.

The separation of nickel from cobalt (Ni:Co = 1:0.28–1:2.81) carried out according to these directions gives faultless results.

In precipitations in which it is desirable to avoid the use of alcohol, the reagent renders good service but has no special advantage over dimethylglyoxime (13), (14).

VI. Nitrosophenylhydroxylamine Ammonium, "Cupferron" (23)

As already mentioned, the importance of Cupferron is not that the metal complexes formed with certain ions can be used as determination forms, but rather the value of the reagent lies in the fact that many separations that are complex and difficult can be very easily carried out.

The numerous publications appearing in the last 20 years on Cupferron are often applications of general separation procedures to special cases. Therefore a thorough study of all reports cannot be included here.

The discoverer of Cupferron, O. Baudisch (23), made only very general statements concerning the use of the reagent; the first exact precipitation procedure was described by H. Biltz and O. Hödtke. These authors used a 6% aqueous solution of Cupferron as reagent.

1. Determination of Iron and Its Separation from Aluminum, Nickel and Chromium (92)

The determination can be carried out in a strong hydrochloric, sulfuric or acetic acid solution.

Determination procedure: The reagent solution at room temperature is slowly poured down the side of the beaker with stirring into the test solution whose volume should be within optimal analytical limits. A red-brown, flocculent precipitate comes out. The end of the precipitation is easily recognized by the appearance of a white finely crystalline precipitate.*

For complete precipitation of the iron it is necessary to have an excess of about one-fifth more than the required quantity (0.833 g. Cupferron for 0.1 g. Fe).

Larger quantities of the precipitate tend to clump somewhat during precipitation but by crushing with a glass rod are easily filtered. After fifteen to twenty minutes the precipitate is filtered out in a platinum cone type of filter using rather weak suction at the beginning and strong suction at the end. The precipitate is washed free of acid with water at room temperature, after this with strong ammonia water to remove the excess of the reagent and at the end again with pure water. It is carefully ignited and weighed as Fe_2O_3.

The results obtained leave nothing to be desired in exactness.

Using the same directions, iron is determined in the presence of aluminum, nickel or chromium only first washing the precipitate with 2N hydrochloric acid, then with water, then with dilute ammonia and at the end again with water.

The same errorless results are obtained in these separations.

For the separation of iron from nickel and cobalt in the analysis of alloys Nissenson (93) gives the following instructions:

1 g. of the alloy is dissolved in concentrated HCl saturated with bromine and the solution evaporated—thus volatilizing the arsenic. The residue is taken up with dilute sulfuric acid and evaporated to the evolution of SO_3 fumes. After cooling, the solution is diluted with water, the lead sulfate filtered off and the solution precipitated with hydrogen sulfide. The solution is again filtered, the hydrogen boiled off and the filtrate oxidized with hydrogen peroxide or ammonium persulfate. After cooling the iron is precipitated by the dropwise addition of an 8% Cupferron solution accompanied by steady shaking.

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* By definition Cupferron is the *ammonium* salt of nitrosophenolhydroxylamine. It is proposed that the *free* nitrosophenolhydroxylamine which forms the characteristic white precipitate in acid solution be called the "*free acid*" of Cupferron. By using an excess of Cupferron, a large quantity of this "free acid" is formed. This crystalline, snow-white precipitate is of considerable value in precipitating and capturing small amounts of metals. At the same time it facilitates the collecting, filtering and washing of the precipitate.

Because of its naphthalene ring, these properties are even more pronounced in the "free acid" of Neocupferron.

2. Determination of Copper: Its Separation from Zinc and Cadmium

The precipitation of copper (92) in a large excess of mineral acids is to be avoided since the copper complex is somewhat soluble in the stronger mineral acids. Precipitation is best done in an acetic acid solution and the free mineral acids present partially buffered with sodium acetate.

The precipitation itself is done according to the directions given for iron. The, at first, finely divided precipitate is allowed to stand and after about ten minutes of vigorous stirring coagulates and settles. In the clear solution the addition of more reagent shows nicely whether the precipitation was complete since no Cupferron is precipitated out of an acetic acid solution. (When working in mineral acid solutions the end of the reaction is not so clear since the copper complex has almost the same color as the free acid of Cupferron.) An excess of the reagent is also necessary for complete precipitation of copper,—double the quantity calculated from the copper present is needed.

The precipitate is filtered out by suction as described in the iron precipitation; first washed with water at room temperature, then with 1% Na_2CO_3 solution to remove the excess of the reagent and finally again with pure water. The precipitate is then carefully ignited to CuO. In order to assure complete change of the copper to the oxide about an hour heating over the blast lamp is necessary.

The separation of copper from zinc (92) is carried out in acetic acid solution and gives equally good results.

The separation of copper from cadmium (92) can be carried out only in weak mineral acid solution and gives, although the copper precipitate is deposited in mineral acid solution rather slowly, very well agreeing results.

J. Hanuš and A. Soukoup (94) who undertook the separation of copper from zinc and cadmium as an exact study recommend the following procedure: The copper precipitate, which is precipitated in an acid solution with an excess of reagent, must be filtered immediately after the formation of the white crystalline precipitate since it again goes into solution if it stays in contact with the acid solution for a longer time.

The cadmium salt is probably quantitatively precipitated out of the exactly neutralized solution but it is not suitable for the determination of cadmium.

Hanuš and Soukoup carry out the separation of copper from cadmium and zinc by precipitating the copper out of a 5–10% sulfuric acid solution with Cupferron and determine cadmium and zinc in the filtrate according to the usual methods.

Since the copper complex is soluble in ammonia, iron can thus be separated from copper (92).

Both metals are precipitated out of a mineral acid solution with Cupferron solution, the precipitate carefully washed with water, then the copper complex removed by washing with concentrated ammonia until the extraction solution is no longer dark blue. Finally the precipitate is washed several times with water. (The precipitate remaining on the filter is treated as usual, igniting and weighing as Fe_2O_3.)

The ammoniacal filtrate is evaporated to remove the most of the ammonia, then acidified with acetic acid and some reagent added. The precipitate is then treated as described for copper.

The values obtained by this method are very satisfactory; however, the iron values are somewhat too high.

3. Determination of Aluminum and Its Separation from Magnesium (95)

A. Pinkus and E. Belche have announced the following procedure: The weakly sulfuric acid solution (0.005N) is precipitated in the cold with 1½ times the Cupferron theoretically required and filtered after several minutes. The precipitate is washed with water containing Cupferron and ignited wet. Alkali salts are not adsorbed by the precipitate, thus accelerating their separation.

The separation of aluminum from magnesium can be done with a single precipitate according to the above directions. The precipitate is washed out of the filter with 0.1N hydrochloric acid which contains about 6 g. Cupferron per liter and then with water containing Cupferron until the chloride reaction disappears. The determination of aluminum in the presence of much magnesium (i.e. 0.1 g. Al_2O_3 with 1 g. $MgCl_2$) gives values which show about 0.3–0.9 mg. too much Al_2O_3. With smaller excess of magnesium the aluminum values are more exact.

The washed and dried aluminum compound is very slightly soluble in dilute acids, and in hydrochloric acid containing Cupferron, the solubility is even less. Since on the other hand, the compounds of chromium, manganese, nickel, cobalt and zinc are very easily soluble in dilute acid, the procedure appears to offer an excellent basis for separating these metals from aluminum. However, experiments relative to this have shown that separations cannot be satisfactorily carried out in this way. When hydrochloric acid containing Cupferron is used, resination occurs. Also the difference in solubility in 0.1N hydrochloric acid is still too small.

4. The Determination of Titanium and Its Separation from Iron, Aluminum, Phosphoric Acid and Uranium

Method: Titanium is quantitatively precipitated in a dilute sulfuric acid solution which contains tartaric acid. Iron is precipitated before the Cupferron precipitation as FeS, so only titanium is precipitated with Cupferron out of the iron free solution. The instructions given by Thornton (96) for this separation have been found by Schwarz-Bergkampf (97) to be very exact. The following method takes into account the slight alterations of Thornton's original method recommended by Schwarz-Bergkampf. 4–6 times more tartaric acid than oxide is added to the solution in a 500 ml. erlenmeyer flask (solution volume should not be more than 100–200 ml.) and the contents gently heated. The solution is exactly neutralized with ammonia, then acidified with 1–2 ml. of 1:1 sulfuric acid and the iron reduced by passing in hydrogen sulfide. This reduction of the iron is absolutely necessary since without it the precipitation with ammonium sulfide carries down part of the titanium. After all the iron is reduced, the solution is made distinctly alkaline with about 30 ml. ammonia and the iron precipitated by passing in hydrogen sulfide under pressure. After standing a short time the precipitate settles, is filtered through a white band filter and washed about ten times with water containing a small amount of ammonium sulfide. The ferrous sulfide filtered off is ignited to Fe_2O_3. 40 ml. of 1:1 H_2SO_4 are now added to the filtrate from the ammonium sulfide precipitation under cooling with flowing water. The universal indicator (Merck) added should already be changed over to the acid side after the addition of the first 10 ml. of the acid. If too much ammonia was added, it is impossible to have the necessary acid concentration for the titanium separation. Thornton recommends that the hydrogen sulfide be driven out by boiling; according to Schwarz-Bergkampf however, this is not necessary since the greatest part of the precipitated sulfur is retained by the titanium precipitate and the colloidal sulfur in the filtrate is entirely dissolved by ammonia. If in spite of this, it is preferred to remove the hydrogen sulfide by boiling, then it is necessary to cool the solution to room temperature. The volume of the solution should now be approximately 400 ml.

The solution is now precipitated in the cold with 10 ml. of 6% Cupferron solution and after the precipitate settles the completeness of the precipitation tested by adding a drop of the reagent. If precipitation is complete, a white precipitate is formed; the filtrate is tested in the same way. The precipitate is deposited in an easily filterable form after strong shaking. It is then filtered, washed about twenty times with 4% hydrochloric acid under light suction and finally freed as well as possible from the wash solution by strong suction. The filter together with the precipitate is dried at 110°, heated in a weighed platinum or quartz crucible first over a very small flame until the end of the first violent smoke evolution and then increasing the flame to full heat to burn the carbon off. Finally the TiO_2 is ignited over a meker burner to constant weight.

In the filtrate, the aluminum can be directly precipitated with oxine-acetate solution after adding about 100 ml. of ammonia and heating to 70°.

C. Mayr and A. Gebauer (98) found that it was not easy to obtain correct aluminum values by this method. By using so much Cupferron to separate the titanium, the aluminum precipitate thrown down by the oxine-acetate solution was somewhat discolored as opposed to the well known bright greenish yellow color of the pure aluminum oxine. So as a result, the values for aluminum are too high. The authors have corrected this error source in the following method which has proven of special advantage in the analysis of Rutile and Ilmenite. The method depends on the fact that ferrous salts form a soluble complex salt with thioglycollic acid of the formula, $Fe(CH_2S\cdot COONH_4)_2$ By adding hydrogen peroxide to this solution and heating to 60–70° the iron is quantitatively precipitated as the oxyhydrate.

Procedure: The mineral fused in the usual way with potassium bisulfate or potassium pyrosulfate is dissolved with cold, 4% sulfuric acid. The iron is now reduced with sulfurous acid and the excess sulfurous acid boiled off. 0.2–2.0 ml. of thioglycollic acid (depending on the iron content) are added to the solution and the solution carefully made ammoniacal using methyl red as indicator. By slowly adding the ammonia, a very distinct change from red to yellow is noticed; another drop of ammonia again forms a red color (formation of the complex compound). At the same time aluminum and titanium start to precipitate as the oxhydrate.

The precipitate is collected on a black band filter (Schleicher and

Schull, 589), dissolved in hydrochloric acid (1:10), reprecipitated and filtered. This alternate precipitation and solution must be continued until the precipitate is pure white—thus free from iron. If this point has been reached, the precipitate is washed with ammonium thioglycollate solution and ignited to constant weight. In this way the sum of the oxides, $Al_2O_3 + TiO_2$ is obtained.

Angeletti (99) **separates titanium from uranium** by precipitating the former with Cupferron in a weak sulfuric acid solution and washing the yellow precipitate obtained with cold water. The uranium is precipitated in the filtrate by ammonia.

L. Silverman (100) proposes the following rapid method for **the determination of titanium in high speed steels:**

A two to five g. sample is dissolved with 50 ml. hydrochloric acid and 100 ml. water in a 400 ml. beaker. If necessary the solution is filtered, diluted to 200 ml. and cooled with ice. Then a 1.5% aqueous solution of Cupferron is added and the solution strongly shaken. After five minutes it is filtered, the precipitate washed with hydrochloric acid (1:10) until the filtrate is colorless and finally the acid removed by washing with cold water. The filter and precipitate are dissolved in 20 ml. concentrated $HNO_3 + 15$ ml. concentrated H_2SO_4 and evaporated twice until white fumes appear. After cooling the solution is diluted with water, 5 ml. hydrogen peroxide (3% H_2O_2) added and the color compared to titanium solution of known content. Iron, chromium and nickel do not disturb the determination but in the presence of vanadium the precipitation must be repeated.

For ores high in iron, W. R. Bennett (101) has worked out the following procedure: In a solution which contains uranium, iron, titanium and aluminum, the iron is removed by electrolysis with a mercury cathode. The decanted solution is evaporated to a volume of about 150 ml. and sulfuric acid added until about 10% by volume is present. By adding potassium permanganate until a very faint red color is obtained all of the uranium is changed into the sexvalent form. The solution thus prepared is now cooled to 60° and precipitated by adding Cupferron dropwise until no more precipitate is formed. The titanium precipitate is washed with cold 10% H_2SO_4 containing about 0.5% Cupferron and ignited to TiO_2.

The excess Cupferron in the strongly concentrated filtrate is destroyed by heating with 10 ml. of concentrated nitric acid until SO_3 fumes are given off and a volume of 5 ml. reached. The solution is diluted and oxidized several times with potassium permanganate in order to change all the uranium into the sexvalent form. The solution is poured through a Jones-reductor and finally the uranium titrated with potassium permanganate.

5. Determination of Bismuth and Its Separation from Silver, Mercury, Lead, Cadmium, Arsenic, Antimony, Chromium, Manganese, Nickel and Cobalt

A. Pinkus and J. Dernies (102) recommend the following method: To the test solution, which should contain not more than one gram—equivalent of HCl or H_2SO_4 per liter, a 5% Cupferron solution of one and a half times the theoretically required amount is added drop by drop. (6 ml. of reagent solution for 1/10 g. Bi_2O_3.) The heavy, flocculent, yellowish white precipitate is filtered in the usual manner and washed with 0.1% Cupferron solution. The precipitate, together with the filter is dried in a porcelain crucible, and slowly heated to 700° until all the carbon has disappeared. In order to convert any metallic Bi which might have been formed during the ashing to the oxide, several drops of concentrated HNO_3 are added. The HNO_3 is smoked off and the residue is again brought to approximately 700° and weighed as Bi_2O_3.

The lead and calcium in the filtrate are quantitatively precipitated in a neutral solution with Cupferron ($1\frac{1}{2}$ times theoretical amount). The other elements are determined in the filtrate by the usual methods.

6. The Precipitation of Gallium and Its Separation from Aluminum, Iron, Uranium and Zinc

For the determination of gallium, L. Moser and A. Brukl recommend the following procedure (103): The neutral solution, which should contain between 0.01 g. and 0.3 g. Ga, is diluted to 200 or 300 ml. with 2N sulfuric acid, and precipitated at room temperature with a 6% aqueous solution of Cupferron; that is, for 0.1 g. Ga, 0.1 g. Cupferron. This is filtered through a paper filter with a platinum cone (under weak suction at the end). 1 or 2 ml. of Cupferron solution are added to the slightly cloudy filtrate and the solution refiltered through the same filter. If the filtrate is not completely clear after the second precipitation the filtrate is once more precipitated with 1–2 ml. of the reagent solution. Then the precipitate is washed under continuous strong suction with 2N sulfuric acid until the chlorides are completely removed (because of the volatility of $GaCl_3$). It is then ignited to Ga_2O_5.

The separation of gallium from aluminum or chromium can be carried out with good results after the above directions. In the filtrate from the gallium precipitation the excess of Cupferron is destroyed by adding hydrogen peroxide and concentrating to the evolution of SO_3 fumes. The aluminum or chromium is precipitated after one of the usual methods. Also, since indium is not precipitated by Cupferron, the separation of gallium from indium can be carried out in this way. A successful separation of gallium from indium depends on carefully washing the precipitate with 2N sulfuric acid which contains several milliliters of reagent solution. The addition of Cupferron to the wash solution is necessary to reduce the solubility of the precipitate. In the presence of a large excess of indium the precipitation must be repeated.

The separation of gallium from cerium offers no difficulties using the above directions.

7. *The Separation of Gallium from Iron, Aluminum and Titanium*

The method is based on the precipitation of gallium out of a sulfuric acid solution containing tartaric acid. According to E. Schwarz-Bergkampf (104), the tendency of gallium to form complex salts make necessary exact control of the precipitation condition. The precipitation of gallium in the presence of tartaric acid is successful only if there is an acid concentration of 6 ml. conc. sulfuric acid in the 400 ml. precipitation volume.

Separation procedure (104): A sufficient quantity of tartaric acid is added to the solution containing iron, titanium, aluminum and gallium. The iron is removed with ammonium sulfide in the way described earlier and the titanium from the filtrate. The filtrate is exactly neutralized by adding 6 ml. concentrated sulfuric acid for every 400 ml. of solution and then cooled with flowing water. The solution so prepared is precipitated with Cupferron and the precipitate coagulated by vigorous shaking. After filtering and washing it is carefully ashed and converted to the oxide by strong ignition.

In a similar manner, H. Pied (105) was able to separate **niobium** and **tantalum** from iron with Cupferron.

The residue obtained after fusion with potassium pyrosulfate is dissolved in water and acidified. The acids of niobium and tantalum (also vanadium) which may be precipitated in this way are dissolved in oxalic acid and the iron precipitated out of the filtered solution with ammonium sulfide in the cold.

The filtrate which contains the niobium and tantalum is strongly acidified with sulfuric acid and the hydrogen sulfide driven out by boiling. Cupferron solution is added to the cooled solution with strong shaking. Niobium and tantalum (together with titanium) are quantitatively precipitated. The precipitate is, after filtration, washed with very dilute sulfuric acid.

According to J. Brown (106) the **separation of iron, titanium and zirconium from aluminum and manganese** can be carried through with excellent results since iron, titanium and zirconium are quantitatively precipitated with Cupferron. The filtrate of the Cupferron precipitation is evaporated with concentrated nitric acid to destroy the precipitant and aluminum and manganese are separated according to the usual methods.

The Cupferron precipitate is converted into oxides by ignition, then fused with potassium pyrosulfate and separated in the usual manner.

W. M. Thornton, Jr. (107) very carefully investigated the precipitation of **thorium with Cupferron.** He showed that very minute amounts of free sulfuric acid prevent quantitative precipitation. However the precipitation is quantitative if done in a solution containing free acetic acid.

N. J. Matwejew (108) **separated iron from thorium** in the following way: A solution of 150 ml. volume to which sufficient tartaric acid is added is made weakly alkaline with ammonia and a slight excess of colorless ammonium sulfide is added. After filtering and washing of the ferrous sulfide with water containing ammonium sulfide, the filtrate is acidified with 5 ml. of dilute sulfuric acid and heated until the hydrogen sulfide is completely removed. After cooling down, 25 g. ammonium acetate are added, the solution diluted to 400–500 ml. and precipitated with 5% Cupferron solution in excess.

Thorium is quantitatively precipitated as $(C_6H_5(NO)NO)_4Th$.

Finally there is still the work of Pinkus and Katzenstein (109) who precipitated **mercury** (I) with Cupferron as well as the work of S. G. Clarke (110) who pointed out the separation of vanadium from tungsten. This last method is worked out especially for the determination of vanadium in steels which contain tungstic acid.

Also the determination of iron and copper in chrome plating baths can according to N. I. Ssurenkow (111) be done directly in the bath solution with Cupferron.

N. J. Matwejew (112) uses Cupferron to analyze pyrites which contain copper.

K. Schröder (113) obtained faultless results in the determination of iron in $K_4Fe(CN)_6 \cdot 3H_2O$ and also recommends the reagent for rapid control of the titer value in analytical iron determinations.

8. The Determination of Tin

A. Pinkus and J. Claessens (114) recommend the following procedure for the determination of tin with Cupferron and its separation from antimony, arsenic, lead and zinc: A solution containing at least 6 g. of tin and at most 1–1.5 gram-equivalents of hydrochloric or sulfuric acid in a liter is precipitated with a 5% aqueous Cupferron solution, using an excess of 1.5–2 times the theoretical amount. A greater excess of Cupferron may cause resination to occur. After several minutes the solution is filtered and washed with a 0.05% Cupferron solution. The precipitate is dried at 60–70° and ignited. According to the authors, the drying of the precipitate is not absolutely necessary. The error in the determination does not exceed several tenths of a milligram.

For the **separation from antimony,** the solution is oxidized with hydrogen peroxide if any antimony (III) is present. Antimony (V) is not precipitated by Cupferron. In the oxidized solution, the tin is precipitated either as described above or below and the antimony precipitated in the filtrate with hydrogen sulfide. The mean error for tin is as little as 0.01% and as little as 0.1% for the antimony.

The **separation of tin from arsenic** is independent of the degree of oxidation. The solution should never contain more than 1 g. equivalent of acid per liter. The tin is precipitated as described above. The arsenic in the filtrate is precipitated as $Mg(NH_4)AsO_4$ and determined as $Mg_2As_2O_7$. The results are almost as exact and as favorable as in the separation from antimony.

In the **separation of lead,** the solution should naturally contain no anions which form insoluble precipitates with the lead. A 0.5–1N nitric acid solution is suitable for the precipitation. The precipitation itself is carried out as described above.

In the **separation of tin from zinc,** the solution must be 1N with respect to the acid. Ammonia is added to the filtrate from the tin precipitation until it has a very weakly acidic reaction. With a small Cupferron excess it is not necessary to destroy the organic material in the filtrate.

By means of Cupferron, alloys such as Sn-Zn-Pb or Sn-Sb-Pb can be easily analyzed.

N. H. Furman (115) also obtained very good results in determining tin with Cupferron. He recommends that the precipitate stand 30–45 minutes with frequent stirring. Then the white emulsion-like form of the precipitate changes into a yellow, solid and easily powdered modification. The precipitate is washed with cold water, dried in a weighed crucible, ignited and weighed as SnO_2.

To separate tin from iron and zinc, one precipitates in the same way, dissolves the coprecipitated iron from the ignition residue in a convenient way and determines the zinc in the filtrate by precipitation with ammonium phosphate.

9. The Determination of Zirconium

W. M. Thornton, Jr. and E. M. Hayden (116) recommend the following procedure for the separation of zirconium from iron and aluminum in steels.

Procedure: 3–5 g. of steel are dissolved in hydrochloric acid, the silicic acid filtered off and treated with hydrofluoric acid. The residue left is dissolved in a little hydrochloric acid and combined with the filtrate out of which most of the iron is removed by shaking with ether. The solution is now oxidized, boiling, 20% carbonate-free sodium hydroxide is poured in to precipitate the aluminum and the solution filtered. The precipitate is dissolved in hydrochloric acid; any zirconium phosphate formed is fused with soda. After removing the phosphoric acid, the residue is dissolved in hydrochloric acid (1 : 1) and finally iron, manganese and nickel are removed from the combined solution by precipitation with ammonium sulfide. Sulfuric acid is added to the filtrate until about 8% by weight of acid is present.

The filtered solution is cooled with ice water and the zirconium precipitated by an 8% Cupferron solution. The precipitate is ashed and fused with soda to separate the vanadium. The titanium obtained can be determined colorimetrically.

According to the investigations of P. Klinger and O. Schliessmann (66) the Cupferron procedure in the zirconium determination must be changed. After shaking out with ether, the solution is immediately precipitated with Cupferron and the precipitate brought into solution by fusion. Then the separation with ammonium sulfide and tartaric is carried out and the zirconium finally precipitated a second time with Cupferron.

G. E. F. Lundell and H. B. Knowles (117) made a detailed study of the different determinations and separations with Cupferron. They drew the following conclusions from this study.

1. The use of Cupferron for the determination of copper is only of theoretical interest and has no practical importance.

2. The determination of iron by Cupferron offers no special advantage over other methods. However, the determination can be very advantageous in many separations, i.e., Fe + Ti from Al + Mn.

3. The separation of titanium and zirconium from phosphoric acid is not so exact as titanium alone from phosphoric acid. This is because zirconium forms a difficultly soluble phosphate.

4. Titanium cannot be separated from vanadium.

5. The separation of titanium and zirconium can only be done when uranium is in the sexvalent form. With uranium (IV) the determination values tend to be too high.

6. The separation of titanium and zirconium from tungsten or from thorium is not feasible.

7. Platinum does not disturb the separation of titanium and zirconium from platinum.

8. Boric acid is not disturbing in the separation of titanium and zirconium from boric acid.

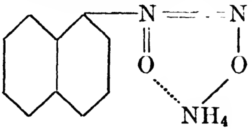
9. The separation of titanium and zirconium from the alkalies. The presence of large amounts of alkalies causes too high results. In this case it is suitable to first precipitate with ammonia, dissolve the precipitate in acid and then to precipitate this solution with Cupferron.

The authors recommend that the Cupferron method should only be used when the approximate composition of the sample is known. Otherwise, it is necessary to analyze the Cupferron precipitate since it may be contaminated with coprecipitated ions. The separation of iron from manganese and of iron and titanium from aluminum and manganese is excellent.

The varied usefulness of Cupferron, which in general gives good results, make the reagent appear to be a valuable aid to analytical chemistry.[*]

NH_4

VIa. Neocupferron (α-nitrosonaphthylhydroxylamine Ammonium)[†]



Recently Baudisch and Holmes (117a) introduced a new reagent, Neocupferron. It is a derivative of Cupferron but not a substitute although it reacts similarly in many cases. The use of Neocupferron is pointed to in certain cases; for instance, in the precipitation of small amounts of metal in a highly dilute solution. Here the precipitate is so voluminous that direct precipitation and separation is possible.

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[*] Compare also A. Tettamanzi, *Ind. Chimica*, **9**, 752; *C.*, 1935, II, 757.

However the use of Cupferron in microanalysis does not seem to be of much use. See R. Strebinger (81).

[†] By Stuart Holmes.

Both the α and the β compounds were prepared. Unlike "Naphthin" they are not interchangeable; they show considerable variation in both chemical affinity and activity. The α compound proved to be more stable and more generally satisfactory.

The authors deal generally with the reagent, pointing out the solubility of the Neocupferron salts of uranium, neodymium and cadmium in organic solvents (Cupferron salts do not react in this way) and they also mention the strong affinity shown by the reagent for the alkali earths. The specific determination of traces of iron and copper is given in detail. This procedure seems to be of practical importance in the analyses of waters since direct precipitation is preferable to the usual concentration methods.

Preparation of Neocupferron: 50 grams of technical α-nitronaphthalene are dissolved in about 1300 ml. of 95% alcohol in a 2 liter flask. The flask and contents are cooled in ice to 0° and the solution saturated with gaseous ammonia. A rapid stream of hydrogen sulfide is then used in place of the ammonia until the flask is filled with golden ammonium sulfide crystals. It is necessary to keep the flask immersed in snow ice or an ice-salt mixture during the entire operation. The flask is allowed to stand in the cold for about 24 hours, then the reaction mixture is poured into a large volume of water and the precipitated, white, α-naphthylhydroxylamine is filtered and washed until it is snow white.

The moist hydroxylamine is dissolved in 500 ml. of ether, the aqueous layer separated and the solution filtered into a one liter, three-necked, round bottom flask. The flask is immersed in snow ice and a mechanical stirrer fitted in one neck of the flask. Gaseous ammonia is admitted through one neck and ethyl or butyl nitrite through the other. (Ethyl nitrite is so easily prepared from hydrochloric acid, sodium nitrite and ethyl alcohol that its use is recommended.) A thick, white precipitate of α-nitrosonaphthylhydroxylamine ammonium is formed which is filtered and washed with ether.

It is important to dry the Neocupferron in an air stream which contains a little ammonia. The pure white, water-soluble salt is then stored over ammonium carbonate and protected from light. Samples kept in the refrigerator were perfectly preserved even after a year.

Determination of iron and copper: The determination of iron in mineral water and sea water is rather unsatisfactory since a large volume of water must be evaporated to a small volume in order to separate the iron. With solutions containing considerable amounts of salt, precipitation or adsorption of iron may take place. Neocupferron allows the direct precipitation of small amounts of iron. (5 mg. Fe per liter gave a fairly voluminous precipitate.)

Determination procedure: 30 ml. of concentrated hydrochloric acid (Sp. Gr. = 1.19) are added to 500 ml. of water and the mixture cooled in ice water. Iron and copper are now precipitated by adding a tenfold excess of Neocupferron solution and the precipitate allowed to stand in the cold for about an hour. (A small amount of filter pulp, S & S ⋇292, facilitates filtration.) The contents are then vigorously stirred for a minute, filtered, using a platinum cone and slightly reduced pressure and washed with ice water. Any traces of calcium and magnesium are removed by washing with 0.7N hydrochloric acid and the precipitate again washed with ice water. Any copper can be separated by washing with 5N ammonium hydroxide. The precipitate is then dried, cautiously ignited in a platinum crucible and weighed as Fe_2O_3. The copper is best determined colorimetrically.

VII. "Thionalid," Thioglycolic Acid-β-amino Naphthalide (24) (25)

In order to make clear and to extend the discussion carried on in the general part concerning this reagent, a summary of the cations which are precipitated by thionalid is given below. From the table it is apparent that the varied reactions of the reagent can be somewhat controlled by "masking." Four groups can be distinguished which are of importance for the **qualitative** detection of the individual ions.

Thionalid precipitates:

1. In mineral acid solution: Cu, Ag, Au, Hg, Sn, As, Bi, Pt, Pd.
2. In solutions made alkaline with soda and containing tartrate: Cu, Au, Hg, Cd, Tl.
3. In alkaline cyanide solutions containing tartrate: Au, Tl, Sn, Pb, Sb, Bi.
4. In alkaline cyanide solutions containing tartrate and sodium hydroxide: Tl.

The precipitations as a whole have a high sensitivity. For cations precipitated out of acid solution, the sensitivity is 1:10,000,000. Thionalid in many respects reacts similarly to hydrogen sulfide. The following discussion compares these two reagents and points out the advantageous use of thionalid to replace hydrogen sulfide for many purposes.

In the first place it is important to mention that thionalid complexes are precipitated formula pure. Because of their high molecular weight, the resultant conversion factor is very favorable and thus the exactness of the determinations is essentially increased. In separations, it is of special importance to prevent induced precipitation of foreign metals. As is evident from the table, the separation of lead and cadmium from the remaining metals of the H_2S group is easily carried out—this is especially valuable in the analysis of alloys. Also the time of analysis is shortened considerably by using the reagent. Since thionalid—in contrast to hydrogen sulfide—is very pleasant to work with and also since the excess of reagent can be simply removed, it should be explicitly noted that the reagent *has the attributes to replace* the usual sulfide precipitations or the use of H_2S in many precipitations.

TABLE 2

Metal	Concentration Limit	Limit of Identification	Color of the Complex
		γ/ccm.	
Cu	1:10,000,000	0.1	Yellow
Ag	1:5,000,000	0.2	Yellow
Au	1:2,500,000	0.4	Yellowish-brown
Hg	1:15,000,000	0.06	White
Sn	1:12,500,000	0.08	White
As	1:100,000,000	0.01	White
Sb	1:40,000,000	0.02	White
Bi	1:10,000,000	0.1	Yellow
Pt	1:10,000,000	0.1	Yellow
Pd	1:10,000,000	0.1	Yellow

So far the publications have dealt mainly with the metals of the first group (118) (precipitation out of mineral acid solution). Table 2 lists the concentration limit and the limit of identification of the individual metals:

The concentration limit and the limit of identification was determined in 5 ml. of solution to which 0.5 ml. of 2N mineral acid was added.

Preparation of the reagent solution: A 1% solution of the reagent in alcohol or glacial acetic acid is used. Since the solution is stable only for a few hours, it is prepared shortly before use. The reagent dissolves easily in most of the organic solvents (methanol, ethanol, acetone, formic acid, glacial acetic acid, pyridine, etc.); it dissolves with difficulty in water acidified with mineral acids. In pure water, thionalid is a little soluble (100 ml. water at 20° and 95° dissolved 0.01 g. and 0.08 g. thionalid respectively). However, the solubility is considerably increased by the addition of alcohol or glacial acetic acid so that hot dilute alcohol or hot dilute acetic acid can be used to wash the precipitate. The effect of alcohol or of acetic acid on the metal complexes is not of great importance if the solution contains not more than 10–15% by volume of alcohol or acetic acid when the precipitation is finished.

Because of the sulfhydryl group, the thionalid is a weak reducing agent. Therefore, oxidizing materials (also ferric salts) must be reduced before the precipitation. Hydroxylamine sulfate is excellent for this purpose.

1. Determination and Separation of Copper (87)

The copper complex precipitated out of a weakly acidic copper solution by thionalid has the composition $Cu(C_{12}H_{10}ONS)_2 \cdot H_2O$. Drying at 105° does not remove the water of crystallization. The precipitation is carried out in a dilute sulfuric or nitric acid solution (maximum acid concentration 0.5N). In weak acid solution (about 0.1N) the presence of chloride (up to 1% of the precipitation volume) does not have an unfavorable effect. Greater amounts cause negative errors. Supposedly copper is partly reduced to the cuprous form by the reagent whereby the precipitation of the Cu(I) halide is possible. If precipitation is done in an acid solution as strong as 0.5N, then the results are too high; one could therefore think that under these conditions the halogen acid of copper is added to the thionalid. From a consideration of these facts, the following **precipitation procedure** is recommended: The solution of the copper salt is heated to about 80–85° and precipitated under stirring with an alcoholic or glacial acetic acid solution of the reagent. About a tenfold excess of the reagent solution is used for precipitation (depending on the Cu present). For example, a solution which contains 0.02 g. Cu in 150 ml. is precipitated with 20 ml. of 1% reagent solution. The precipitate, coagulated by stirring, is filtered hot through a glass filter crucible which was warmed before filtration by sucking through hot water. (The warming of the crucible is necessary in order to prevent the eventual clogging of pores of the sinter plate by the reagent.) The precipitate is washed acid free with hot water and dried at 105° to constant weight.

F = 0.1237; log F = 9.09237–10.

During the filtering and washing, the precipitate is never sucked completely dry since then the precipitate plugs the pores of the filter and the filtration takes place very slowly.

The results obtained are excellent.

In this way copper can be faultlessly separated from thallium, iron, calcium, barium, magnesium, zinc, cadmium, manganese, cobalt, nickel, chromium, lead and aluminum.

1a. Volumetric determination of copper: The precipitate obtained in the usual way is filtered through a filter wet with hot water and washed free of acid with hot water. The precipitate together with the filter is now transferred to the beaker in which the precipitation took place, stirred with 50 ml. of glacial acetic acid and 4–5 ml. of 5N sulfuric acid and about 0.1 g. of potassium iodide and 10 ml. of about 1N ammonium thiocyanate solution added to it.* An excess of an 0.02N iodine solution is now added, the solution diluted with water and the excess of iodine back titrated with 0.02N thiosulfate solution.

1 ml. of 0.02N thiosulfate solution ....1.27 mg. Cu.

In place of the unstable iodine solution it is recommended to use the stable potassium iodate solution.

To separate copper from the metals not precipitable by thionalid in acid solution, the copper is precipitated out of a large volume (about 200 to 300 ml.); ferric salts and oxidizing agents must be reduced before the precipitation.

In the presence of chlorides it is not feasible to reduce the ferric iron or the oxidizing substances present since Cl′ ions are very favorable to the formation of Cu (I). These Cu (I) ions usually cause negative errors. In such a case, it is advisable to remove the hydrochloric acid by fuming with sulfuric acid. The cooled solution can then be diluted with water and precipitated as described above.

Removal of the reagent from the filtrate: Approximately 0.5N iodine-potassium-iodide is added dropwise to the warm solution (70–80°) under stirring until the yellow color is permanent. The solution is cooled to room temperature and the precipitated dithionalid filtered off. In the filtrate, the other metals can now be determined according to one of the optional methods.

The determination of copper as well as the accompanying metals gives faultless results.

2. Determination and Separation of Silver (*118*)

The determination of silver out of pure silver salt solutions with thionalid offers no advantage compared to the methods in use.

The precipitation with the reagent is, however, very much recommended for the separation of silver from thallium and lead—especially in those separations which offer great difficulties according to the methods now in use.

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* Compare G. Bruhns, *Chemiker Ztg.*, **42**, 301 (1918).

Separation procedure: Exactly the same procedure as was announced for the separation of copper from thallium, etc., is used here. However the silver complex cannot be weighed since it is already decomposed at 100°. The complex is filtered through a paper filter, ignited to metallic silver, and eventually transposed into the chloride and weighed in this form. The check analyses published show great exactness.

2a. Volumetric determination of silver: The titration is carried out in the way described for copper only omitting the addition of the thiocyanate.

1 ml. 0.02N thiosulfate solution..........2.158 mg. Ag.

3. Determination and Separation of Mercury (118)

The mercury complex corresponds to the formula $Hg(C_{12}H_{10}ONS)_2$ and is precipitated according to the formula only by following these conditions:

1. The Cl′ ion concentration of the solution should not be greater than 0.1N. Otherwise the results are too high.
2. The nitric acid solution of mercuric nitrate must be changed over into the chloride: An amount of chloride equivalent to the mercury present is added to the solution. Sulfates are not disturbing.
3. For precipitation, a threefold excess of the reagent is used.

The precipitation itself is carried out in the way described for copper; the precipitate is filtered through a warmed filter crucible (IV) and the precipitate dried at 105°.

$F = 0.3169$; $\log F = 9.50098-10$.

The **separation of mercury** from the other metals is carried through according to the same directions. For the reduction of the oxidizing materials one must add an alkali chloride in order to change the mercury over into mercuric chloride, which is, as is well known, stable against hydroxylamine sulfate. The check analyses give excellent results.

3a. Volumetric determination of mercury: For the iodometric titration of mercury the same directions given for silver are followed. The volumetrically obtained values are very exact.

4. Determination and Separation of Bismuth (118)

Bismuth can be precipitated in nitric acid as well as in sulfuric acid solutions. The bismuth complex, $Bi\ (C_{12}H_{10}ONS)_3 \cdot H_2O$, precipitates first milky and cannot be filtered until it has stood for ½ hour on the water bath. During this time it is coagulated and crystallized. The acid concentration most favorable for coagulation of the precipitate is 0.1N. In the presence of chlorides or sulfates, however, a 0.2N mineral acid solution is necessary because with a lower acid concentration a basic bismuth salt would be precipitated.

Since the formation of the basic salt does not occur in pure nitrate solutions, two precipitation procedures result.

α-Precipitation of bismuth out of chloride and sulfate free nitric acid solutions: Ammonia or sodium hydroxide is added to the solution until the turbidity is permanent, then 3–5 ml. of 2N nitric acid added and the solution diluted with water to 100 ml. The solution so prepared is precipitated according to the general directions with a fourfold reagent excess, placed in a covered beaker on the water bath for 20 to 30 minutes and the coagulation of the precipitate accelerated by frequent shakings. During the standing on the water bath, the precipitate originally milky yellow, becomes an intensive lemon yellow.

If the supernatant liquid has become clear, then the precipitate is filtered through a warmed glass filter crucible (IV) and after washing, dried to constant weight at 100°.

β-Precipitation of bismuth out of acid solutions containing chloride and sulfate: 10 ml. 2N sulfuric or nitric acid are added to the solution neutralized with ammonia or sodium hydroxide, the solution diluted to 100 ml. with water and precipitated as announced under α. Immediately after the precipitation, the solution is neutralized by adding 5 ml. of 2N sodium hydroxide for each 100 ml. of solution. The precipitate is then treated as described under α.

F = 0.2387; log F = 9.37785-10.

In the presence of large amounts of chloride, the bismuth results are low since the bismuth is partly bound through the formation of a halogen acid complex and thus its determination cannot be accomplished.

4a. Volumetric determination of bismuth: Since bismuth iodine uses thiosulfate, the usual iodometric titration must be modified. By adding purest (iron free) ammonium chloride to the solution, the titration can be carried out without trouble. The bismuth complex is bound by the ammonium chloride and can now be titrated according to the directions given for mercury. However, care must be taken that the solution remains saturated with ammonium chloride.

4b. Separation of bismuth from other metals: These separations are carried through according to the directions for the individual determinations. Only for the **separation of bismuth from large amounts of lead** are certain precautions necessary. The neutralized solution is diluted to about 200–400 ml., 5–6 ml. 2N nitric acid added for each 100 ml. of solution and the solution again precipitated as in α or β. Naturally, if ferric salts are present here, they must also be reduced in the usual way. It should be noted that through long standing of the bismuth solution on the water bath, the ferrous salt is in a small part again oxidized. The ferric salt so formed now oxidizes part of the reagent to dithionalid. Thus the precipitate when finally filtered cannot be weighed on drying. Therefore the bismuth precipitate is filtered through a paper filter, the filter together with the precipitate dried at 100° and the filter ashed separately in a weighed porcelain crucible. The remaining precipitate is now transferred to the crucible and after adding 1–2 g. of sublimated oxalic acid, ignited—first over a small flame and finally for five minutes with the full Bunsen flame.

It should be mentioned, however, that the volumetric determination can be carried out with equally great exactness (according to the filtration method).* For the volumetric determination a 1% reagent solution in glacial acetic acid is used. The solution is standardized empirically with a determined amount of metal as follows (118):

The mineral acid solution to be determined is heated to about 80°–90° and the reagent solution allowed to flow in out of a burette until, in a filtered sample, no further turbidity is noticed by adding another drop of reagent. By this test titration the approximate value of the volumetric solution is determined. In the next titration the exact value can be found by using very small drops at the endpoint. In this case, it is necessary to pour the solution several times through the same filter and then again titrate. Otherwise errors can arise through adsorption of traces of metallic ions by the filter paper.

4c. Separation of bismuth from other metals from solutions made alkaline with soda and containing tartrate and cyanide (119): According to the following method, bismuth can be separated from Cu, Ag, Cd, Hg, As, Pt, Pd, Fe, Co, Zn, Ni, Cr, Ti and Al; according to the procedures so far worked out, vanadium also does not appear to be disturbing. The sensitivity of the precipitation is about 1:10,000,000.

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* Hans Th. Bucherer: *Z. anal. Chem.*, **52**, 297 (1920). A simplified volumetric method for the quantitative determination of acids and bases which tend to form insoluble, or practically insoluble salts.

In an alkaline solution, bismuth is precipitated by thionalid forming a bright yellow precipitate, Bi $(C_{12}H_{10}ONS)_3$, which does not contain any water of crystallization—and which is suitable for weighing.

Separation of bismuth from the above mentioned metals:* The precipitation is very similar to lead (115). Since the bismuth thionalid is very soluble in acetone, the following procedure must be adopted for washing the precipitate. The precipitate, washed free from cyanide, is washed with small portions of 10% alcohol until the filtrate shows no turbidity when tested with iodine solution. The precipitate is then dried at 105° and weighed.

$F = 0.2436$; $\log F = 9.38668-10$.

In the presence of very large amounts of accompanying metals, the following procedure is recommended. The precipitate is dissolved in acetone, 100 ml. of 5% potassium cyanide solution containing 2 g. sodium tartrate added and the acetone boiled off. After cooling the above procedure is followed.

5. *The Determination and Separation of Lead* (*119*)

The lead complex precipitated out of a solution made alkaline with soda and containing cyanide and tartrate has the formula, Pb $(C_{12}H_{10}ONS)_2$. The bright yellow precipitate prepared in this way contains 32.40% Pb. Since the precipitation of lead by thionalid has no special advantage in the individual determination, only the separation procedures are considered: 10–20 ml. of 20% sodium tartrate solution (for 0.5 g. sample, 4 g. sodium tartrate) are added to the mineral acid, sulfate free solution of the metal salts and 2N sodium carbonate added to a phenolphthalein end point. Then the necessary amount of potassium cyanide solution to form complexes with metals which react with potassium cyanide is added.† After this, sufficient sodium carbonate solution is added to make the solution about 1N. The precipitation volume should be within the analytical limits (100–300 ml., depending on the amount of foreign metals present). The solution is precipitated with 3–4 times the amount of precipitant theoretically necessary (for 0.025 g. of Pb, about 0.15–0.2 g. of the reagent in 8–10 ml. of alcohol). The reagent solution is added in a fine stream to the cold lead solution with vigorous stirring and the solution heated to boiling with gentle stirring. The boiling clarifies the liquid which is originally milky because of the finely divided precipitate and after a short time the precipitate takes on a granular crystalline structure and a pure, bright yellow color. The solution is cooled to room temperature by placing the beaker in cold water and then filtered through a glass filter crucible, G4. With steady whirling, the precipitate (it should not be sucked tight to the fritted glass plate) is washed cyanide free with cold water until the filtrate shows no reaction with silver nitrate. In order to remove any occluded thionalid, the precipitate is washed several times with small portions of 50% acetone. The washing with acetone is continued until a sample of the filtrate diluted to 4 times its volume does not show any turbidity (dithionalid) when acidified with sulfuric acid and several drops of 0.1N iodine solution added to it. The precipitate is dried at 105° to constant weight.

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* Au(III), Pb, Sn(IV), Th(IV), Sb(III) and the alkaline earths are disturbing.

† For 0.5 sample, 40–50 ml. of 20% potassium cyanide solution.

F = 0.3240; log F = 9.51055–10.

Chlorides are disturbing if the Cl^- concentration is over 4%; the sulfate ion content must be less than 1%.

By following this procedure, lead can be successfully separated from Ag, Cu, Zn, Co, Ni, Al and Fe(III); also the precipitation is not influenced by the presence of As(III), Cd, Cr(III), and Ti(IV).

6. Separation of Antimony from Fe(II), Co, Cr(III), Ti(IV) and Ce(III) (119)

The antimony complex precipitated by thionalid has the composition $Sb\ (C_{12}H_{10}ONS)_3$ corresponding to an antimony content of 15.81%. The precipitation has a sensitivity of about 1:2,500,000. This sensitivity is considerably lessened in the presence of foreign metals which must be masked with potassium cyanide. Thus a separation from Pb, Th, Au, Bi and Sn is not possible. Similarly, the presence of As, Cd, Hg and the alkali earths is disturbing to the separation.

The precipitation procedure is the same as just described for lead only here the precipitate, just as in the bismuth precipitation, must be washed with 10% alcohol.

F = 0.1581; log F = 9.19893–10.

7. The Determination of Thallium (120)

As already mentioned on pages 15 and 86, only thallium is precipitated quantitatively in solutions made alkaline with sodium hydroxide and containing tartrate and cyanide. The thallium complex is precipitated as a lemon yellow, crystalline compound which is insoluble in acetone and has the formula, $Tl\ (C_{12}H_{10}ONS)$.

The method makes possible—by observing the necessary conditions—

the separation of Tl from Ag, Cu, Sb, Pt, Pd, W, Mo, Pb, Hg, Bi, Cd, As, Sn, V, Zn, Te, Co, Au, Ni, Al, U, the alkali earths and the alkalies.

The sensitivity is 1:10,000,000.

a. Precipitation of thallium out of pure thallium salt solutions:

Determination procedure: The acidic thallium salt solution (containing 0.025–0.1 g. Tl) is neutralized with 2N sodium hydroxide and 2 g. of sodium acetate and 3–5 g. potassium cyanide added to it. Now 10–20 ml. of 2N sodium hydroxide is added so that the solution is approximately 1N and the solution diluted with water until the volume is about 100 ml. A 4–5 fold excess of thionalid (acetone solution) over the amount theoretically necessary is now added to the cold solution. The solution is heated to boiling with gentle stirring until the amorphous precipitate is changed into the crystalline form and the solution is clarified. Since the thallium complex is somewhat soluble when hot, the beaker is immersed in cold water and cooled to room temperature.

The precipitate is filtered through a fritted glass filter crucible, G4, washed cyanide free with cold water and then free of thionalid with acetone. The precipitate is dried at 100° and weighed.

$F = 0.4860; \log F = 9.68664 - 10.$

The values obtained are very exact.

b. Determination of thallium in the presence of other metals: It is essential in the separation procedure that not more than 5 g. of potassium cyanide and 5 g. of sodium tartrate per 100 ml. be present. For example, if 10 g. of potassium cyanide per 100 ml. is added, the thallium values are too low.

In the presence of other metals such as Cu, Ag, Hg, Au, Cd, Zn, Te, Co, Ni, etc., it is necessary to have a high potassium cyanide content in order to form complexes between the metals and the cyanide ions. Also in this case the hydroxyl concentration is lowered and must be adjusted to 1N by adding more 2N sodium hydroxide.

c. Separation of thallium from Ag, Cu, As, Sb, Sn, W, Mo, Zn, Al, Co, Ni and Fe(II):

Solutions and reagents needed: 1. A 5% acetone solution of thionalid. Since this solution is decomposed on standing a few hours, it is recommended to always prepare a fresh solution.

2. Sodium tartrate solution: 20 g. sodium tartrate in 100 ml. water.

3. 2N sodium hydroxide.

4. Potassium cyanide solution: 20 g. c.p. potassium cyanide in 100 ml. water.

Separation procedure: 10–25 ml. of sodium tartrate solution are added to the thallium solution for each 100 ml. present and the solution neutralized with 2N sodium hydroxide to a phenolphthalein end point. Then enough 20% potassium cyanide is added to obtain a 5% concentration of it in the solution. Now the alkalinity is adjusted to 1N with 2N sodium hydroxide and the solution precipitated in the cold with the 5% reagent solution using a 4–5 fold excess of reagent over the amount theoretically necessary (e.g. for 0.1 g. Tl about 0.4–0.5 g. thionalid in 8-10 ml. of acetone). Then the solution is heated to boiling with gentle stirring whereby the finely divided milky precipitate is coagulated and the liquid clarified. By the boiling, the bright yellow metal complex takes on an intensive lemon yellow color and becomes crystalline in structure. The solution is cooled to room temperature by immersion in cold water and then filtered through a fritted glass filter crucible, G4. It is important not to suck the precipitate tight to the fritted glass plate since then it is difficult to wash out foreign particles. The precipitate is first washed cyanide free with cold water and then with 2–3 ml. portions of acetone until the filtrate no longer contains any thionalid (sample diluted 2-3 times with water, acidified with sulfuric acid and an iodine solution added. If thionalid is present, dithionalid is formed; see page 15). The precipitate is dried at 100° and weighed.

The check analyses published show excellent agreement with the theoretical values.

α. Separation of thallium from Fe(III), Cd, Au, Pt, V and U:

Preparation of the solution: Iron (III), which is changed to an oxidizing agent, potassium ferricyanide, by the addition of potassium cyanide, must be reduced by boiling with a reducing agent such as a hydroxylamine salt and changed into the ferrocyanide complex before adding the reagent in order to prevent oxidation of the thionalid. After the reduction and cooling to about 30°, the thallium can now be precipitated.

As with Fe(III), the noble metals, Au, Pt, Pd must also be reduced with hydroxylamine to prevent oxidation of the reagent.

In the separation from large amounts of vanadium it is necessary to reduce the vanadium to prevent some precipitation of the difficultly soluble thallium vanadate.

In the separation from cadmium it is necessary to raise the cyanide content to 7–9% (for about 0.2 g. Cd in a total volume of 100 ml.) since the cadmium cyanide complex can dissociate and form cadmium ions. By using this cyanide concentration the cadmium is complexly bound and its coprecipitation prevented.

In the separation from uranium present as the uranyl salt, it must be noted that the uranyl ion can not be kept completely in solution by adding tartrate to the alkaline solution since sodium uranate precipitates out in the hot solution. This can not be prevented by raising the cyanide concentration since the uranyl salt does not form a stable complex with cyanide ions. Probably the sodium uranate can be again brought into solution by adding ammonium carbonate but in hot solutions the uranium complex is not completely stable. It is recommended that before beginning the washing process as described under α, the precipitate should be washed with 10% ammonium carbonate.

By following this procedure, the analysis of ores and crude metals containing thallium can be carried out with good result.

β. *Separation of thallium from mercury, bismuth and lead:* The precipitation procedure described under α can not be used when mercury, bismuth and lead are present since then they are partially coprecipitated.

However, a separation from these metals is possible because of the solubility of these metallic thionalates in acetone. The general precipitation procedure is changed only in that here a 10 fold excess of reagent is added which is dissolved in enough acetone to bring the final acetone concentration in the solution to about 30% (if mercury is present, the potassium cyanide addition must be raised to 9 g. KCN for each 100 ml. of solution). The determination is then continued as described above.

γ. *Determination of thallium in the presence of the alkaline earths and magnesium:* The disturbing effect of these metals depends on the insolubility of the alkali earth carbonates and of magnesium hydroxide in solutions made alkaline with sodium hydroxide and containing tartrate. However, in ammoniacal, carbonate-free solutions, thallium can be separated from alkali earths without difficulty:

Procedure: CO_2-free ammonia is added to the weakly acid solution until the alkalinity is 1N (if magnesium is present, ammonium chloride must also be added). The separation can then be done as already described.

d. *Volumetric determination of thallium:* The thallium is precipitated exactly as described for the gravimetric determination, filtered through a white band filter (Schleicher and Schull, # 589^2), washed with water and acetone and the filter and precipitate returned to the original precipitation beaker. A mixture of 3 parts of glacial acetic acid and 1 part of 2N sulfuric acid is then poured over the precipitate in order to dissolve the complex (for 0.01-0.04 g. of precipitate about 40 ml. of the acid mixture). 0.02N iodine is then added until the yellow color of the free iodine indicates an excess and after the mixture is well stirred, it is back titrated with 0.02N thiosulfate.

1 ml. 0.02N iodine solution = 4.09 mg. Tl.

e. *Micro analytical determination of thallium* (*121*): The principal problem in determining small amounts of thallium was in working out a colorimetric method. The method is based on the reducing effect of thionalid and its metal complexes on phosphomolybdic and phosphotungstic acids, forming a blue oxide of molybdenum or tungsten. (Compare with page 15.)

Solutions and reagents needed:

1. For precipitation:
   Freshly prepared 10% potassium cyanide solution
   Freshly prepared 5% solution of the reagent in acetone
   Purest acetone
2. For the colorimetric determination:
   1N sulfuric acid
   96% alcohol
   Phosphotungstic-molybdic acid solution:

1 g. phosphomolybdic acid, 5 g. sodium tungstate, 5 ml. conc. phosphoric acid (d = 1.70) and 18 ml. water are refluxed in a flask with a ground glass joint for about 2 hours and, after cooling, the solution is diluted to 25 ml.

Purest formamide
A color scale of the standard solution:

Since the blue color of the thionalid and this heteropolyic acid is unstable, the comparison solution can only be prepared in an artificial way.

Preparation of the comparison solution: Known amounts of thallium are precipitated with thionalid, as described below, then dissolved and the solution reacted with the heteropolyic acid mixture for 15 minutes at 40°. The samples show a blue color of different intensity—depending on the amount of thallium present.

By mixing aqueous solutions of Chicago blue, naphthylamine black and a trace of India ink, it is possible to match the color tone. With small amounts of thallium, 5–15 γ's, the color can be matched with a

0.01% indigo solution to which a trace of the above color stuff has been added. These standard solutions keep a long time in tightly stoppered bottles protected from light. The thallium value can be estimated within about 20% of the exact value. The solutions can not be compared directly in a colorimeter on account of their different optical properties.

Determination procedure: 0.5 ml. of 2N sodium hydroxide solution and 0.5 ml. of 10% potassium cyanide solution are added to the very weakly acid or neutral solution of the unknown (the unknown should have a volume of about 3–5 ml. and, after adding the sodium hydroxide, should be alkaline in reaction). The solution is placed in a centrifuge tube and precipitated with 5–6 drops of the reagent solution. The milky precipitate is changed to the crystalline form by heating on the water bath at 90° for 5 minutes and stirring constantly; the change in structure can be noted by the change in the color of the precipitate to a pure, deeper yellow. Then the solution is cooled and rapidly centrifuged. The supernatant liquid is then removed as completely as possible with a capillary tube (the precipitate settles very firmly against the bottom and side walls so that no noticeable loss occurs from the washing process). The precipitate is washed twice with 3–5 ml. portions of acetone, rotating the tube around so that the walls are thoroughly washed and then again centrifuging. The thallium complex is practically insoluble in acetone. Then the wash solution is removed, the precipitate dissolved with 2 drops of 1N sulfuric acid and 1 ml. of alcohol (heating gently if necessary) and the solution transferred to a colorimeter tube. The centrifuge tube is rinsed out once with 1 ml. of warm alcohol and once or twice with 1 ml. of warm water.

1–3 drops of the phosphotungstic-molybdic acid solution—depending on the quantity of the precipitate—and 30–40 drops of formamide are added to the solution and after shaking vigorously for 15 minutes at 40°, the solution is allowed to stand. It can then be compared to the above described standards and the thallium content approximated (±20%).

For an exact determination, a second sample of the unknown and a standard thallium solution corresponding exactly to the estimated quantity of thallium present are both treated as just described and the blue colors compared in a colorimeter.

The results are very exact. The method can also be used to determine other metals which can be precipitated by thionalid. However, the precipitate is then washed only with hot water and dissolved with pyridine. The rest of the procedure is exactly the same.

8. Nephelometric Determination of Copper, Mercury and Arsenic (117)

Copper, mercury and arsenic can be determined by the nephelometric method if no other metals of the mineral acid thionalid group are present (see page 86; Ag, Sb, Sn, Au, Pd, and Bi can be determined in a similar manner. A 1% solution of thionalid in glacial acetic acid is used as reagent solution.

Determination procedure: 5 drops of 2N sulfuric acid are added to the metal salt solution to be determined (the volume should be about 15 ml.), the solution heated to boiling and about 3 drops of the reagent solution added. At the same time, a standard solution containing as nearly as possible the same metal content as the unknown is precipitated under the same conditions. After 2–3 hours—with very small amounts 5–6 hours—the turbidity is compared in a nephelometer. The average of 5 readings is taken for the metal value.

The check analyses published by the authors show very exact values.

A potentiometric titration of thallium by means of thionalid has been described by R. Berg and E. S. Fahrenkamp (122).

VIII. α-Nitroso-β-Naphthol (26) (27)

The reagent (26) though known for a long time, was not correctly established in analytical practice until a short time ago. This was because the precipitate when precipitated according to the directions of Ilinski and v. Knorre, did not come down formula pure. Also the ignition of the precipitate to the metal gave no satisfactory values. The precipitation procedure first worked out by C. Mayr and F. Feigl (27) was successful in producing a formula pure compound which could be used for direct weighing.

Preparation of the reagent (27): 4 g. of the reagent are dissolved in the cold by digestion with 100 ml. of glacial acetic acid and to this solution 100 ml. of hot, distilled water are added. The filtered solution can be used immediately.

1. Determination procedure (27)

The weakly acid solution of cobaltous salts, which should contain not more than about 300 mg. cobalt, is concentrated to about 10–20 ml., allowed to cool and 5–10 drops of perhydrol added to the cold solution. 2N sodium hydroxide is now added until the $Co(OH)_3$ precipitates. Because of the strong oxygen evolution it is advantageous to precipitate in a covered beaker. 10–20 ml. of glacial acetic acid are now added and the precipitate brought into solution under gentle warming. Then the volume is brought to about 200 ml. with boiling hot water and the cobalt precipitated with 10–20 ml. of the reagent solution. Now, under strong stirring the solution is heated to boiling, continuing until the precipitate is coagulated. The supernatant liquid over the quickly settling precipitate is colored yellow and is completely clear. The precipitate is now filtered through a porcelain filter crucible dried at 130°. The remainder of the precipitate is transferred into the crucible with 33% acetic acid and the precipitate washed three times with hot acetic acid. Finally, it is washed four times with nearly boiling water and dried at 130° to constant weight. $F = 0.09649$; $\log F = 8.98447-10$.

Limit of identification: 0.05 γ Co.

Concentration limit: 1:1,000,000.

Time of determination: about two hours.

Greater amounts than about 25 mg. cobalt should not be determined in this way, since the drying of larger amounts of precipitate requires several hours before constant weight is reached.

Finally, an example of the practical application of the described method is given.

a. Analysis of Rinmans green (27): A 0.3–0.4 g. sample is weighed into a 50 ml. beaker, 10 ml. of water added, the sample brought into solution by adding 0.4–0.5 ml. of concentrated sulfuric acid and the precipitated silicic acid filtered off. After cooling, five drops of perhydrol are added and the solution made alkaline with sodium hydroxide. Now 40 ml. glacial acetic acid and 40 ml. water are added and the cobalt precipitated with about 6–8 ml. of reagent solution. In filtrate, which is first evaporated to small volume to remove most of the acetic acid, the organic matter is destroyed by evaporating to dryness twice with fuming nitric acid. After complete destruction of the organic matter the nitrates are changed into chlorides by evaporating twice with hydrochloric acid. The precipitate is dissolved with several drops of hydrochloric acid and water, made ammoniacal and then saturated warm with hydrogen sulfide. The solution is acidified with acetic acid, the zinc sulfide filtered off and then determined according to Rose.

The faultless results and the simplicity and rapidity of operation point to the advantageous use of this method in comparison to the usual gravimetric and volumetric methods for cobalt.

b. Determination of cobalt in ores: A. Craig and L. Cudroff (123) propose the following method:

1 g. of ore is dissolved by successive treatment with 10 ml. of nitric acid, 10 ml. of hydrochloric acid and 10 ml. of sulfuric acid and the solution fumed 3 times with sulfuric acid. After cooling, the residue is dissolved with 75 ml. of water and 10 ml. of hydrochloric acid, the solution boiled and any blackish residue present is filtered off and washed with dilute hydrochloric acid. This residue is fused with potassium bisulfate and the aqueous solution of the fusion combined with the filtrate. Hydrogen sulfide is now passed in the solution, the sulfides filtered off and the hydrogen sulfide removed by boiling. The iron is now oxidized with hydrogen peroxide and removed by the double acetate precipitation. The cobalt is precipitated in the strongly acetic acid filtrate as described above.

In carrying out this procedure it is important to notice that nitrates or nitric acid should not be added and that Sn, Cu, Ag, Bi, Cr and Fe must be removed. Ni, Zn, Al, Ca, Mg, Pb, Cd, As and Sb have no effect.

The original procedure provided for the determination of cobalt as Co_3O_4; by using the method of Mayr and Feigl (27) the exactness of the determination is increased.

2. Determination of Palladium and Its Separation from Platinum

W. Schmidt (124), who first proposed the determination of palladium with nitrosonaphthol, ignited this precipitate to metallic palladium and weighed it. If however, a palladium solution is precipitated in the manner described below then the formula pure compound, $(C_{10}H_6ONO)_2Pd$, is obtained.

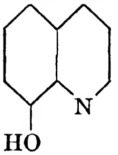
Determination procedure (30): To the palladium solution, whose volume should be about 20 ml. and which should contain about 30 mg. palladium, 10 drops of perhydrol are added and after this sodium hydroxide until the reaction is alkaline. Now 30 ml. of glacial acetic acid are added, the solution diluted to about 150 ml. with hot water, heated to boiling, and then precipitated with 15 ml. of 1% reagent solution. The red brown, flocculent precipitate is filtered through a filter crucible washed first with 20% acetic acid and then with boiling hot water until the filtrate comes through almost colorless. The precipitate is dried at 135° to constant weight.

F = 0.2367; log F = 9.37417–10. The determination is very exact.

3. Determination of Palladium and Its Separation from Copper and Iron

M. Wunder and V. Thüringer (125) recommend the following procedure: The solution, which contains the three metals as their chlorides (the iron is in the ferric form), is brought to a volume of about 150 ml., 20 ml. of conc. hydrochloric acid and 20 ml. of glacial acetic acid are added and the solution heated to boiling. Now a freshly prepared, saturated at boiling temperature solution of the reagent in 50% acetic acid is gradually added in small portions; first a red color is formed which changes during the continued boiling into a red, voluminous precipitate. The addition of the reagent is continued until no red color is formed with a drop or two of the reagent. The precipitate floats on the surface of the solution and the liquid underneath is yellow, caused by ferric salts and the excess of the reagent. The precipitate is filtered while still hot to avoid contamination with iron. The precipitate is washed with hot, 5% hydrochloric acid, then with hot water and the filter and precipitate dried in the oven. The dry filter is ashed carefully over a small flame (sublimated oxalic acid is usually needed to complete the ashing), the spongy metal obtained reduced in a stream of hydrogen and allowed to cool in a stream of carbon dioxide.

IX. 8-Hydroxyquinoline, "Oxine"*



M.P. = 75°

M.W. = 145

Since its introduction into analytical practice by R. Berg (126), 8-hydroxyquinoline, or oxine, has become a familiar and widely used reagent for determining metals and even non-metals (127). The sensitivity, the ease of operation as well as the accuracy obtainable by either volumetric or gravimetric methods has led to numerous publications concerning this reagent—a complete review will be found in Berg's book (128).

HO
H_2O
$(H_2O)_3$

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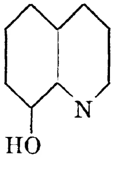
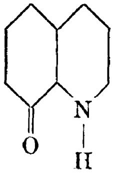
* By Stuart Holmes.

Oxine has the empirical formula, C_9H_7ON. Theoretically two structural formulas are possible:



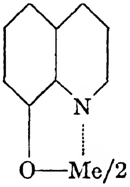
(I)



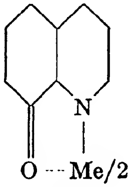
(II)

Pure oxine crystallizes in nearly colorless needles and is soluble in organic solvents. In the presence of small amounts of water, the colorless solution changes to a yellowish color. This is very probably caused by a change into the quinoid form (II).

Oxine reacts with metal ions to form more or less intensively colored compounds (129) which belong to the inner complex group. In these inner complex compounds, the residual affinity of the metal atom is bound coordinatively to either the nitrogen atom (III), or to the oxygen of the carbonyl group (IV), thus forming a stable 5-membered ring:



(III)



(IV)

Oxine is not at all a specific reagent. In most cases, the hydrogen of the hydroxyl group is replaced by an equivalent of the element in question (Fig. III). In certain cases, the hydrogen may be replaced by a basic group such as TiO^{++}. Mercury, thorium and uranium also react abnormally.

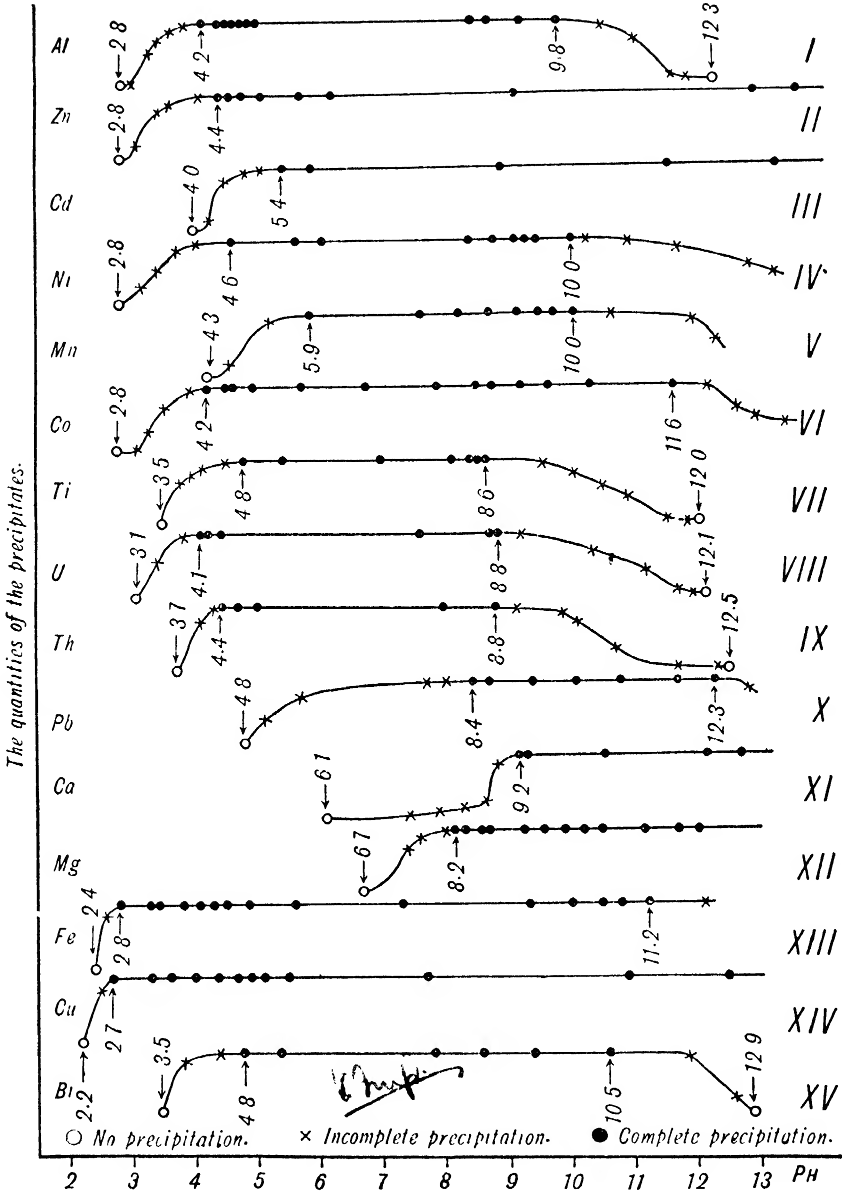
Despite the non-specificity of the reagent, it does have some very advantageous applications. Often elements are precipitated at a definite pH but are soluble at other pH values. Thus by controlling the pH, the solubility may be sufficient to make valuable separations (130, 131). Certain "masking" reagents may also be used.

The pH range where precipitation occurs and separations are possible may be roughly divided into three groups:

a. The acetic acid-acetate group: By varying the amount of acetic acid and sodium acetate added, the pH of the solution may be adjusted

TABLE 3

The Effect of pH on Precipitation (130)



to any value between 2 and 6. In some cases, the use of ammonium acetate instead of sodium acetate may be advantageous.

b. The ammoniacal group: By using ammonia and tartaric acid or sodium tartrate it is possible to adjust the pH of the solution to any value between 6 and 10.

c. The sodium hydroxide group: This is, of course, merely an extension of the above group. If a higher OH concentration is desirable for precipitation or separation, sodium hydroxide is used instead of ammonia.

For illustration, a precipitation study of zinc (130) is reproduced in Table 4.

TABLE 4

Precipitation of Zinc

Acetic Acid	Sodium Acetate	Sodium Tartrate	Ammonium Hydroxide (2N)	Sodium Hydroxide 2N	pH	Error
ml.	*g.*	*g.*	*ml.*	*ml.*		*mg.*
10 (3N)					2.84	no ppt.
10 (3N)	0.2				3.10	−9.87
10 (3N)	0.4				3.40	−2.63
10 (3N)	0.6				3.60	−1.67
10 (3N)	1.0				4.08	−0.15
5 (1N)	2.0				5.16	0.01
		1.0			6.18	0.10
		1.0	1.0		9.11	0.08
		2.0		5.0	12.96	0.05
		2.0		20.0	13.60	0.02

A disadvantage in using oxine is that the reagent is not very soluble in water. It is however, soluble in alcohol or acetone and in acetic acid. Since the determination of the individual metals is carried out either in acetic acid or alkaline solution, a 2–4% alcoholic oxine solution is used for precipitating alkaline solutions and a 3–4% oxine-acetate solution is used for precipitating acid solutions. When precipitations must be made in neutral solutions, an acetone reagent solution is recommended. The higher solubility of the acetone solution tends to prevent any coprecipitation of the reagent.

Although a general precipitation procedure for all cases is not possible, there are certain guides which may be helpful.

1. An excess of the reagent is necessary for complete precipitation; in acetic acid the solution becomes yellow and in alkali the solution is orange-yellow when an excess of the reagent is present.

2. In general, the solutions are generally heated to about 60–70° for

about 5 minutes. This is generally sufficient to crystallize and coagulate the precipitate.

3. Sometimes the filtrate becomes turbid. This is usually because of the smaller solubility of the oxine in the cold or it may be that an excess of the reagent was not used. If, on warming, the filtrate does not become clear, more reagent must be added.

4. Generally it is sufficient to wash the precipitate with hot water until the filtrate comes through colorless. Sometimes, however, particularly in separations, a special wash solution is advantageous.

5. The excess of oxine can be easily removed by adding ammonia to the filtrate and evaporating. This is an advantage since ignition or evaporation with a sulfuric acid-nitric acid mixture is necessary to remove most of the organic reagents.

Determination procedures: The precipitate can be treated in a number of ways. It may be mixed with oxalic acid and ignited to the metal oxide. Because the metal complex has a very definite structure, it is preferable to dry at 105° and weigh. In some cases the complex retains water of crystallization. If this water of crystallization is unknown or unstable, the complex can be heated to 130–140° and weighed as the anhydrous compound. Since oxine can be so easily brominated, an excellent volumetric method has been developed (132).

Procedure: The metal complex is dissolved in 2N hydrochloric acid, a drop or two of methyl red added and then a standard bromide-bromate solution added from a burette until the color changes from red to yellow. About 1–2 ml. excess of the bromide-bromate solution is now added and then an excess of potassium iodide solution. Usually a chocolate brown precipitate is formed. A standard thiosulfate solution is now added from a burette until the chocolate color dissappears, some starch solution added and the solution titrated to the end point.

In special cases the filtration method of Bucherer and Meier (133) or the acidimetric titration method of Hahn (134) may be advantageously utilized.

Both the gravimetric and volumetric methods have been applied to the micro determination of metal ions (135). The techniques of both Pregl and Emich have been applied with good results. In general about 0.5–3.0 mg. of metal can be determined.

INDIVIDUAL DETERMINATIONS

1. Zinc (136)

Zinc is quantitatively precipitated by oxine from pH 4.6–13.4 as a greenish-yellow complex. On drying at 105°, it is weighed as

$Zn(C_9H_6ON)\cdot 1\frac{1}{2}H_2O$. F = 0.1118. Because the zinc-oxine complex does have a somewhat indefinite water content, the volumetric method is recommended.

In acetic acid-acetate solution (pH 5–6), zinc can be separated from the alkalies, the alkaline earths, lead (137) and manganese (138). In alkali solution, separation from aluminum, $chromium^{III}$, $iron^{III}$, $antimony^{V}$, $arsenic^{V}$, bismuth, cobalt, nickel and manganese is possible. Zinc can be determined in the presence of mercury in alkaline solution by masking the mercury with potassium cyanide and tartaric acid (136).

2. Magnesium (139)

Magnesium is precipitated in alkaline solution (pH > 8.5) but not in acid solution. The greenish-yellow, crystalline precipitate contains water of crystallization on drying at 105° corresponding to the formula, $Mg(C_9H_6ON)\cdot 2H_2O$. F = 0.0698.

Determination procedure: Sufficient ammonium chloride to prevent the hydroxide from precipitating and then several ml. of concentrated ammonia are added to the solution. The solution is then heated to 60–70° and precipitated with an excess of 2% alcoholic oxine solution. When an excess of oxine is reached, the supernatant liquid becomes intensively yellow in color (ammonium-oxine). The precipitate is then filtered through a fritted glass filter crucible, washed with hot ammoniacal water, dried at 105° and weighed. F = 0.0698.

The precipitate may also be dissolved in 2N hydrochloric acid and titrated.

1 ml. $KBrO_3$..........0.000304 g. Mg.

If a higher pH is necessary for separations, 2N sodium hydroxide is used instead of ammonia.

In general, sodium, potassium, lithium and ammonium salts do not interfere (140).*

The determination of magnesium in the presence of calcium, strontium and barium depends on the insolubility of the magnesium-oxine complex in hot ammoniacal solutions while the other alkaline earths are very soluble. By using double precipitation, Berg (139) obtained very well agreeing results.

The filtration method of Bucherer and Meier (133) gives very satisfactory values for this separation, particularly in the rapid determination of magnesium in cements. Redmond (141) also recommends oxine for determining magnesium in cements.

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*The separation of magnesium and lithium salts is practically complete with one separation ((139), see also (140)).

3. Aluminum (142) Al.

Aluminum is precipitated in acetic acid-acetate solution and in ammoniacal tartrate solutions (pH 4.2–9.8). The greenish yellow aluminum complex corresponds to the formula $Al(C_9H_6ON)_2$.

Determination of aluminum in acetic acid solution:

Procedure: The weakly mineral acid solution which should contain not more than 100 mg. of aluminum oxide is diluted to 100–150 ml. and 15 ml. of 3–4% oxine-acetate solution added for each 50 mg. of aluminum oxide. (The use of an alcoholic oxine solution generally results in low aluminum values.) Then the solution is heated to boiling, placed on a boiling water bath, and 2N ammonium acetate solution slowly added with stirring. As soon as the solution becomes turbid, the addition of ammonium acetate is stopped and more reagent added until the precipitate becomes crystalline. Now about 25 ml. more ammonium acetate solution is added and the precipitate allowed to coagulate and settle on the water bath for about ten minutes more. The precipitate is filtered on a fritted glass filter crucible (G3), washed with hot water and then with cold until the filtrate becomes colorless, dried at 130° and weighed. $F = 0.0587$.

The precipitate may be dissolved in equal parts of 10% hydrochloric acid and alcohol, diluted with water and titrated with standard bromide-bromate solution (143).

For separations, it is often advantageous to precipitate the aluminum from an ammoniacal solution. After adding tartaric acid, sufficient ammonium chloride to prevent the precipitation of aluminum hydroxide is added and the solution neutralized with ammonia. The solution is then heated to about 60–70° and the aluminum precipitated with a 2–3% oxine-acetate solution. A little more ammonia is required, but care should be taken not to add too large an excess since it has an unfavorable effect.

To separate small amounts of aluminum from larger amounts of magnesium, precipitation in an acetic acid solution is recommended. To separate small amounts of magnesium from larger amounts of aluminum, the magnesium is first precipitated in a sodium hydroxide-tartrate solution and the aluminum determined in the filtrate (142).

Ferrous ions can be masked with potassium cyanide and the aluminum determined in ammoniacal solution (144). In a similar way T. Heczko (145) has worked out a method using potassium cyanide and hydrogen sulfide for determining aluminum in the presence of iron, manganese, nickel, cobalt, copper, chromium and molybdenum.

In ammonical solution aluminum can also be separated from niobium, tantalum, vanadium, titanium and molybdenum.

4. *Titanium* (*143*) Ti

Titanium reacts with oxine in acetic acid and in ammoniacal solutions (pH 4.8–8.6) forming an orange-yellow precipitate corresponding to the formula, $TiO(C_9H_6ON)_2 \cdot 2H_2O$.

In acetic acid solution, titanium can be determined in the presence of the alkalies and the alkaline earths. By adding malonic acid, aluminum can be masked and the titanium then determined.

Since titanium is soluble in sodium hydroxide-tartrate solutions, separation from the metals which precipitate in this group is possible.

5. *Manganese* (*146*) Mn.

Manganese is precipitated out of very weak acetic acid-ammonium acetate or neutral solutions as a crystalline yellow compound corresponding to the formula, $Mn(C_9H_6ON)_2 \cdot 2H_2O$. Because the precipitate tends to decompose somewhat on drying, particularly at higher temperatures, the volumetric method is recommended.

Manganese can be separated from zinc by precipitating the zinc in a 3% acetic acid solution and determining the manganese in the filtrate by precipitation with oxine. In a similar way, copper and manganese can be separated.

6. *Copper* (*147*) Cu

Copper is precipitated by oxine in acetic acid, ammoniacal and sodium hydroxide solutions (pH 5.33–14.55) forming a green colored complex corresponding to the formula $Cu(C_9H_6ON)_2$. $F = 0.1808$.

In acetic acid solution, copper can be determined in the presence of beryllium, magnesium, calcium, cadmium, lead, arsenic and manganese. In sodium hydroxide-tartrate solution, copper can be determined in the presence of aluminum, lead, tin^{IV}, arsenic^{V}, antimony^{V}, bismuth, chromium^{III} and iron^{III}.

7. *Beryllium* (*148*) Be

Beryllium reacts with oxine in ammoniacal tartrate solution but the precipitate is of little use for analytical purposes because it does not have a definite composition.

However, beryllium does not react with oxine in acetic acid solution and thus it can be easily separated from the metals which precipitate in acetic acid-acetate solutions. The separation of aluminum-beryllium, copper-beryllium and iron-beryllium is of special significance.

8. Iron (146) Fe .

Oxine reacts with iron to form a dark green, water free complex corresponding to the formula, $Fe(C_9H_6ON)_3$. F = 0.1144.

In the presence of an alkaline acetate, iron can be precipitated in fairly high acid concentration (about 15–20% acetic acid). In sodium hydroxide-tartrate solutions, the iron is very soluble.

In acetic acid solution, iron can be determined in the presence of the alkaline earths and the alkalies. Conversely, in sodium hydroxide-tartrate solutions, magnesium can be determined in the presence of iron and aluminum (also the other alkaline earths).

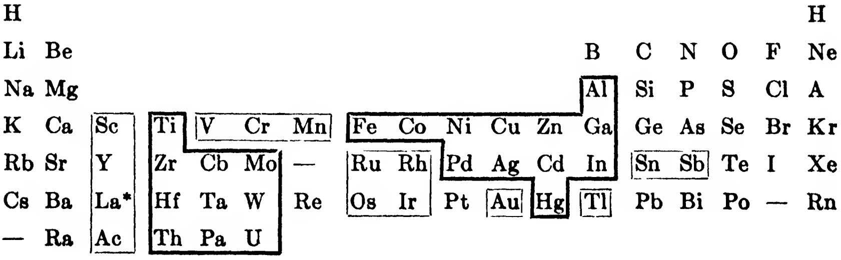
Iron can be determined in the presence of aluminum by masking the aluminum with malonic acid and precipitating the iron in acetic acid solution (146). Very well agreeing results were obtained but in titrating iron precipitates it is necessary to add phosphoric acid to prevent the disturbing effects of Fe^{+++} ions on the iodometric titration.

A few of the more general uses of oxine have been very briefly discussed. However, there are many uses and procedures which could not even be mentioned since they are beyond the scope of this book. Berg and his coworkers have published numerous papers in the *Zeitschrift für analytische Chemie*; in America, Lundell and Knowles have done much to utilize oxine in analytical practices (*B. S. Jour. Research*); Kolthoff and Sandell have made important publications in the *J. Am. Chem. Soc.* For those interested in special application and detailed methods, a perusal of these journals should be most helpful.

In order to show the varied elements that may be precipitated by oxine, the following table is reproduced from Lundell and Hoffman's "Outlines of Methods of Chemical Analysis."

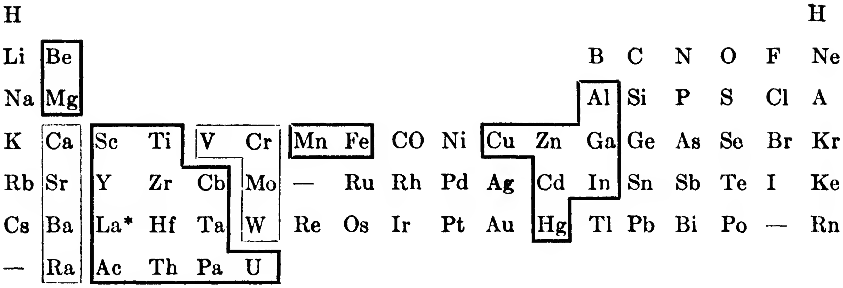
Precipitations by 8-hydroxyquinoline:

A. In acetic acid-acetate solutions:



H																	H
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

B. In ammoniacal solutions:



H																	H
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	CO	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Ke
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks denote partial precipitation, heavy blocks complete precipitation.

X. Mercaptobenzthiazol (28)

Preparation of the reagent: Saturated (5%) solution of the preparation in alcohol purified according to page 17 is used.

1. The Determination of Copper: Its Separation from Cadmium, Cobalt, Nickel, Manganese, Zinc, the Alkali Earths and Magnesium (28)

The solution of the copper salt exactly neutralized with ammonia is warmed and then an excess of reagent solution added. The solution is heated until the orange-yellow, flocculent precipitate coagulates, and the liquid is clear. The hot liquid is filtered through a paper filter, washed with hot water and the filter together with the precipitate dried at 110–120°. The dried precipitate is ignited in a weighed crucible until constant weight is reached.

In spite of the exactly agreeing test analysis announced by Spacu and Kuraš, the objections, as expressed in detail on page 18, must be made against the method.

The separation of copper from about 5–6 times the amount of nickel, cobalt, manganese, zinc and cadmium is carried out exactly as in the above mentioned directions. Since the precipitations with this reagent are so excellent, its use is recommended especially for separations. It should be especially noted that the solution must be exactly neutralized for the separation procedure.

2. The Determination of Cadmium (149)

Ammonia is added in excess to the cadmium salt solution until the precipitate beginning to come down is completely dissolved and then an ammoniacal solution of the reagent is added to this solution. A thick, milky turbidity immediately forms which is changed by stirring or by gentle warming into a white, crystalline precipitate. The precipitate is filtered out in a filter crucible, washed with water containing ammonia and dried at 110°–120° to constant weight. About ½–1 hour is generally sufficient. $F = 0.2330; \log F = 9.40264-10$.

2a. Separation of Copper from Cadmium

An alcoholic reagent solution is added to the exactly neutralized solution of both metal salts as described for copper. The copper salt is filtered off and washed well with hot water. In the filtrate the excess mercaptobenzthiazol might eventually crystallize, but the following determination of cadmium is not disturbed since it is easily soluble in ammonia. To the filtrate from the copper precipitate an excess of ammonia is now added and the cadmium salt precipitated by stirring. If there should be no excess of mercaptobenzthiazol in solution, then several milliliters of the ammoniacal reagent solution are added. The precipitate procedure announced for cadmium is then followed.

The results announced by the authors are very satisfactory. The possibility of using the separation procedure is, however, somewhat limited, since the metals which are precipitated with mercaptobenzthiazol, and those which form insoluble hydroxides with ammonia, must first be removed. Also the presence of nickel and zinc has proven disturbing for the separation.

3. Determination of Lead (150) Sn.

An ammoniacal solution of mercaptobenzthiazol forms two kinds of salts with lead ions—a normal, yellow salt that corresponds to the formula $(C_7H_4NS_2)_2Pb$ and a white, basic salt of the composition, $(C_7H_4NS_2)_2Pb \cdot OH$.

The basic salt is precipitated out of the hot neutral solution as a white, needle-formed, crystalline precipitate which becomes a light yellow by drying at 110°.

The normal salt, which is obtained by precipitation in the cold, is never formula pure, but always contains basic salt. By boiling with concentrated ammonia it can be completely changed into the basic salt.

From the discussion it is apparent that only the basic salt can be used for quantitative analysis although lead is completely precipitated in the cold.

Determination procedure: The aqueous neutral lead solution is heated almost to boiling and an ammoniacal reagent solution added to this solution in excess. (The reagent solution contains 1 g. mercaptobenzthiazol in 100 ml. of 2.5% ammonia.) For best results, this solution is allowed to flow in a drop at a time out of a burette into the hot lead solution under steady stirring. The white precipitate formed is collected in a filter crucible and washed well with 2.5% ammonia. The precipitate is dried at 110° to constant weight, whereby it becomes slightly yellowish. F = 0.5309; log F = 9.72501–10.

For precipitation, at least three times the theoretical amount in the form of a 1% reagent solution must be used (for 0.1 g. $Pb(NO_3)_2$, 20 ml. of reagent solution). If the precipitate should be yellow from small amounts of coprecipitated normal salts then several milliliters of concentrated ammonia are added, and the solution heated until the precipitate is completely white.

Since by working in the cold and also in warm acid solutions the yellow salt is precipitated, acid solutions must first be neutralized with ammonia before heating and precipitating. The results are very good.

4. The Determination of Thallium (150) Tll.

Thallium salt solutions form a sulphur yellow, microcrystalline precipitate with ammoniacal mercaptobenzthiazol of the composition $C_7H_4NS_2Tl$. Since the salt, especially in the warm, is noticeably soluble in water, the precipitation must be done in the cold and in solutions not too diluted. For quantitative precipitations, at least three times the theoretical amount of reagent is required.

Determination procedure: To the thallium salt solution, whose volume should be 30 ml. at the highest, three times the calculated amount of a cold, freshly prepared, 1% ammoniacal solution is added dropwise from a burette. The precipitate is filtered out through a filter crucible, washed thoroughly with 30 ml. of a 2.5% ammonia and dried at 110° to constant weight.

F = 0.5517; log F = 9.74167–10.

5. The Determination of Bismuth (150)

Bismuth is precipitated by mercaptobenzthiazol forming a chrome yellow salt which corresponds to the formula $(C_7H_4NS_2)_3Bi$. Regardless of whether one precipitates with an alcoholic or with an ammoniacal reagent solution the precipitate always contains $Bi(OH)_3$ and can therefore, not be directly weighed. The precipitate must be ignited to Bi_2O_3.

Determination procedure: An excess of alcoholic reagent solution is added to the acid bismuth solution and then dilute ammonia until the smell of it just predominates. (The addition of ammonia is necessary because the bismuth salt is somewhat soluble in dilute acids.)

The solution to which the ammonia was added is now heated until the flocculent precipitate coagulates. It is then filtered through a quantitative filter, washed with a freshly prepared 0.5% solution of mercaptobenzthiazol in 2.5% ammonia and the precipitate together with the filter dried at 110°. As much as possible of the dried precipitate is transferred into a weighed porcelain crucible, the slight residue remaining dissolved off the filter with dilute nitric acid and the solution placed in the crucible. The solution is evaporated to dryness and ignited first with a small flame and later with a full flame, to Bi_2O_3. The check analyses announced show very good agreement.

6. The Determination of Gold (150) Au

Gold salt solutions form a yellowish white precipitate, $(C_7H_4NS_2)_3Au$, with alcoholic mercaptobenzthiazol. However, the precipitate is always contaminated with reagent. Thus it must be ignited to metallic gold. The results obtained with this method are, according to the announcements of the authors, just as satisfactory as those obtained by the usual methods. However, the determination needs much less time and offers the possibility of separation from the metals which are not precipitated by mercaptobenzthiazol.

XI. Pyrogallol (30) (31)

The pyrogallol used for precipitation must, of course, be tested for purity. For this purpose, the melting point of the doubly sublimated product (131°) is determined.

To test for inorganic contamination, 1 g. of pyrogallol is ignited in a weighed platinum or quartz crucible; the pyrogallol should sublimate without weighable residue. To test for tannic acid, 2 g. pyrogallol are dissolved in 5 ml. of ether ($d = 0.720$). In the absence of tannic acid a clear solution results.

1. Determination of Antimony; Its Separation from Arsenic (30)

To the solution, which must contain the antimony in the trivalent form, a little more than the calculated amount of sodium potassium tartrate is added in order to prevent the formation of basic salts during dilution. A solution of nearly five times the theoretical amount of pyrogallol dissolved in 100 ml. of water is added all at once to this solution and the solution diluted to 250 ml. with water. The at first clear mixture becomes turbid after about one-half to one minute and then forms a thick moire type of precipitate which quickly settles. The precipitate is allowed to stand two hours, then filtered through a filter crucible and washed in the crucible two to three times with 50 ml. portions of cold water. This suffices in most cases to remove the excess of pyrogallol. The precipitate is dried at 100°-105°, then after weighing, washed several times with water, redried and checked for constant weight.

F = 0.4601; log F = 9.66285-10.

The washing of the precipitate should not be continued until the filtrate no longer shows a yellow color on making alkaline with a base and shaking. This pyrogallol test possesses such great sensitivity, 1:3,300,000, that a content of pyrogallol corresponding to the solubility of the antimony pyrogallolate is sufficient to prevent a completely negative test.

The **separation of antimony from arsenic** can be done according to these directions without difficulties. In the filtrate from the antimony precipitation, the arsenic can be directly precipitated with hydrogen sulfide. Since the values obtained throughout show sufficient exactness, the method appears suitable to replace the wearisome method of Neher and Bunsen.

2. Determination of Bismuth: Its Separation from Lead (31)

The precipitation of bismuth is only quantitative when the hot solution is not stronger than 0.1N in relation to free acid. The precipitation can be carried out in hydrochloric, nitric or sulfuric acid solution.

Determination procedure: Dilute ammonia is added dropwise to the acid bismuth salt solution until a lasting turbidity arises. This is again brought into solution through the addition of a drop of dilute nitric acid and the solution diluted with water. A concentrated solution of pyrogallol in water is now added and the solution boiled for a short time. A heavy, finely crystalline, yellow precipitate settles out which can be filtered through a filter crucible after short standing. The precipitate is first washed with 0.1N nitric acid, then with pure water and dried at 110° to constant weight.

F = 0.6295; log F = 9.79901-10.

According to Ostroumov (151), should this precipitate be of an amorphous type which is difficult to filter and which darkens rather easily by standing on the water bath, it is probably changed in its composition. The author proposes the following modification of the determination: The weakly acid (nitric) bismuth solution is warmed, neutralized with dilute ammonia, carefully acidified with dilute nitric acid and to the hot solution a slight excess of pyrogallol solution added. Thereby, the yellow precipitate of tiny crystals is immediately formed and under these conditions, should be precipitated formula pure. The solution is now boiled, diluted with water if necessary to replace that lost by evaporation and, after the precipitate has settled, is then filtered.

Separation of bismuth from lead: According to the announcements of Feigl and Ordelt (31) this separation gives excellent results regardless of the ratio of the two metals.

XII. Dithizon (33)

The determinations possible with this reagent can, as already mentioned, be placed in three groups: (1) gravimetric, (2) volumetric, and (3) colorimetric determinations.

1. Gravimetric Determinations (33)

These determinations shall be considered only very briefly since their use is scarcely ever recommendable. The reasons for not using gravimetric determination methods have already been presented in detail in the introduction. It may be mentioned that zinc can be precipitated out of acetic acid solution by dithizon as a red precipitate of the composition $(C_{13}H_{12}N_4S)_2ZnO$. Zinc can be separated from manganese because only zinc is precipitated by dithizon out of 30% acetic acid solution; in the filtrate the manganese can be precipitated as manganese ammonium phosphate.

This procedure does not possess practical significance, it is mentioned only to illustrate the many varied uses of the reagent.

2. Volumetric Determinations

Before considering the individual determinations, the idea of "non-specificity" must be discussed. The non-specificity is measured as the number of elements or element groups which may also react with the reagent under the reaction conditions and disturb the test. For example, if under the determination conditions, there are two other elements in addition to the one sought, which may also react, then the test has a non-specificity of 2. A specific reaction therefore, has a non-specificity of 0. Table 5 is a list of the elements which form complexes with dithizon under various determination conditions and of the conditions which regulate the non-specificity of the reagent.

It is apparent from the table that the cyanide ion in weak acid solution entirely masks the formation of a complex with gold. Also, the thiocyanide ion prevents the formation of the stable complexes with silver and palladium. Thus in the presence of both cyanide and thiocyanide, gold, silver and palladium are masked.

Of the halogen ions, Cl^- and Br^- in large excess are effective in masking silver but not mercury. I^- however, masks both metals.

The non-specificity can be reduced even more with different reaction conditions as shown in Table 6.

TABLE 5

Existence of Dithizon Complexes under Different Reaction Conditions

Reaction Conditions	Reacting Metals (Keto Complexes)
CN', weakly acid	Pd, Hg, Ag, Cu
SCN', " "	Au, Hg, Cu
$CN' + SCN'$, weakly acid	Hg, Cu
Cl', " "	Pd, Au, Hg, Cu
I', " "	Pd, Au, Cu

General principles for the titration procedures (34): The titration is carried out in a separatory funnel. First, a sample titration to approximate the end point is carried out by shaking the aqueous solution with a determined volume of reagent solution (CCl_4). If the carbon tetrachloride layer still shows the color of the pure dithizonate of the respective metal, it is separated and the extraction continued using determined volumes of reagent solution until a greenish, mixed color in the carbon tetrachloride solution shows that the end point has been passed.

Colors of the individual elements with dithizon:

Cu
- alkaline solution = brown
- acid solution = violet

Ag
- neutral or weak alkaline solution: red violet floc insol. in CCl_4
- weak acid solution: yellow in CCl_4 layer

Au weak acid solution: light brownish yellow

Hg
- strong acid: always orange yellow
- weak alkali—violet red: in weak acid or in presence of Hg excess—mixed color

Bi	orange yellow
Co	blue tinged carmine red
Zn	neutral, or at most weakly acetic acid—purple red
Ni	brick red
Cd	strawberry red
Mn	red, very similar to Zn
Pb	strawberry red, similar to Cd

In this manner the approximate position of the end point can be located so that one can very sharply determine the end point by a second titration through the addition of small portions of reagent (0.1–0.2 ml.) in the end point range. For better recognition of the transition point and in order to simplify the separation of small amounts of reagent solution, the reagent solution is diluted with pure CCl_4 and, after the separation of the CCl_4 layer, the solution is washed with pure carbon tetrachloride.

TABLE 6

Specificity of Elements with Dithizon under Different Conditions

Metal to Be Detected	Reaction Condition	Interfering Elements (Non-specificity)
Lead	Neutral solution	14
	KCN solution	2(Sn, Tl)
	KCN solution oxidized beforehand	0
Copper	Alkaline solution	4(Ag, Hg, Au, Pt)
	Acid solution	5(Ag, Hg, Au, Pt, Pd)
	Acid solution + KCNS	3(Au, Hg, Pt)
	Acid solution + KI	3(Au, Pt, Pd)
	Acid solution + KCNS + KCN	2(Hg, Pt)
Silver	Alkaline solution	2(Hg, Au)
	Acid acetate solution	4(Hg, Au, Pt, Pd)
Cadmium	Neutral solution	8
	Alkaline solution	3(Hg, Ag, Cu)
	Alkaline solution + $HONH_2HCl$	1(Cu)
Mercury	Mineral acid solution	3(Pd, Au, Cu)
	Mineral acid solution + KCN + KCNS	1(Cu)
	Formic acid solution	2(Pd, Au)

Preparation of the titer solution: A solution of 3–5 mg. dithizon in 100 ml. of pure carbon tetrachloride is standardized against a solution of known metal content. By storing in a dark flask under 1% sulfuric acid (152) (see especially page 3 of this reference) the titer of the solution is practically stable for several weeks.

Since the dithizon on the market always contains small amounts of yellow colored oxidation products, the reagent must be purified before use. For this purpose a concentrated solution in carbon tetrachloride is prepared (about 20 mg. dithizon dissolved in 100 ml. CCl_4) and then shaken with very dilute ammonia (1 part conc. ammonia to 200 parts water). Only the dithizon is taken up by the dilute ammonia, the impurities remaining in the carbon tetrachloride solution. The carbon tetrachloride layer is separated and fresh carbon tetrachloride poured under the ammoniacal solution. By acidifying, the dithizon is now liberated and immediately dissolved in carbon tetrachloride by shaking. This solution is washed many times with distilled water and now contains the dithizon in a sufficiently pure state. The solution is best stored under sulfurous acid in a brown bottle. Before titrating, a sufficient volume is separated from the sulfurous acid, washed several times with distilled water and finally diluted with CCl_4 to about three times the volume.

a. The determination of silver (152)

Dithizon forms a yellow complex salt with silver in weak nitric acid solutions. The reaction is suitable to determine silver in the presence of all metals which do not react with dithizon. Fairly exact determination can also be carried out in the presence of Pb, Zn, Cd, As, Sb, Bi, Cu and Au. The determination of silver in the presence of mercury cannot be carried out directly since both dithizonates are similarly colored. For the determination of relatively small amounts of mercury, a procedure could however be evolved that still showed sufficient exactness.

Preparation of the reagent solution: The solution should contain approximately 2–4 mg. dithizon per 100 ml. A sufficient amount of the purified solution* stored under sulfuric acid is separated from the acid in a separatory funnel and filtered through a dry filter into a small brown bottle.

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* According to a private communication from Dr. H. Fischer to the editor, it is not very desirable to cover the reagent solution with sulfurous acid for the determination of the rather easily reduced noble metals (Ag, Au, Hg); in this case the acid must first be carefully washed out in order to prevent the disturbing reducing effect.

Determination of the titer of the reagent solution: A silver solution of known content is taken since the titer of very dilute silver solutions (about 12 per ml.) diminishes noticeably with time. Therefore, a weak nitric acid solution of higher concentration (about 0.24 mg. Ag per ml.) is used. This solution is diluted with absolutely chloride free distilled water and may be used for one to two days.

All reagents of course must be absolutely free of chlorine and may contain no mercury or gold. Traces of copper are not disturbing, only the transition yellow to green is replaced by a transition to a red violet (compare with the determination of silver in the presence of copper). The nitric acid used must be free from nitrous acid since this would oxidize the dithizon to a yellow color.

Titration procedure: The titration is best done in weak nitric acid solution. However, under certain circumstances, diluted sulfuric acid could also be used. The solution should contain approximately 15% by weight of nitric acid (about 2.5N). To 10 ml. of a nearly neutral silver solution, about 2 ml. of dilute nitric acid is added. One proceeds exactly as in the standardization of the known silver solution.

The approximate position of the end point is determined as in the earlier described sample titration. After each shaking, the mixture is allowed to settle and the CCl_4 solution separated in a test tube. Thus, the color of the preceding extraction can be compared with each succeeding color. When the end point has been approximated, the titration is repeated. First larger portions are added with vigorous shaking until enough reagent has been added to be just short of the end point (from the sample titration, it is known that this point will give a pure yellow color signifying a slight excess of silver). After separation of the carbon tetrachloride solution, the aqueous layer is now washed with a little pure CCl_4 and more reagent solution added in small portions. The size of these additions is dependent upon the amount of reagent already used and the exactness desired. The additions are measured so they are 1–2% of the amount of the reagent already added. These additions are made from a micro burette which is excellent for measuring these small amounts. Before each addition of reagent solution about 0.02–0.5 ml. of pure CCl_4 (depending on the amount of reagent solution added) are added which forms a layer underneath the solution to be tested. The mixture is then vigorously shaken for about one-half minute and separated. After the separation of the dithizon solution, it is always washed with pure carbon tetrachloride. The titration is continued until the first appearance of a green color. The last portion of the reagent solution added to change the color is divided in half, added to the reagent solution already used and this volume taken as the end point of the titration (152, p. 8). The change of color is easily recognized after a little experience, however, it is worth recommending that pure yellow dithizonate solution in about the same dilution be prepared for comparison. In order to avoid errors through evaporation of CCl_4 or from the dithizon becoming resinous, care should be taken that the burette is not placed in sunlight or near an oven; in certain circumstances the use of a burette of brown glass is recommendable.

The determination of silver in the absence of other metals gives values whose agreement is satisfactory throughout. A silver content of 0.01–0.001% can easily be determined according to these directions.

b. The determination of silver in lead (152)

The determination depends on the fact that lead does not react with dithizon in acid solution. Only in the presence of larger amounts of lead (over 3000 mg./10 ml.) the red color characteristic for lead appears. The determination of silver in the presence of large amounts of lead is possible since the lead reaction first begins after all the silver is converted into the dithizonate. Then not the green color of dithizon but a red or pink color is the end point. By exactly following the working method explained in detail for the silver determination and adding acid as announced below, the recognition of the end point offers no difficulties.

To the nearly neutral lead solution, 2 ml. of dilute nitric acid (about 2.5N) are added for solutions containing about 200 mg. Pb/10 ml., 3 ml. for solutions containing 500–1000 mg. Pb/10 ml. and 5 ml. in the presence of 2000 mg. Pb/10 ml.

For the determination of silver of the order of magnitude of 10^{-2}–10^{-5}%, one must shake especially well, since otherwise the pink mixed color appears too soon. By longer contact of both phases, the lead dithizonate replaces the traces of silver present in the CCl_4 phase and the CCl_4 solution becomes yellow again.

c. The determination of silver in zinc (152)

Practically the same procedure is used here as for the determination of silver in lead. In the presence of 22 mg. of Zn, the red zinc color is obtained by extraction of the weakly acid solution (smaller amounts of zinc do not react). However, this zinc excess destroys the silver determination. It is possible, according to the announcements of the authors, to, in spite of these defects, determine silver contents of the order of magnitude of 6.61×10^{-2}–8.3×10^{-4}% with sufficient exactness.

d. The determination of silver in cadmium (152)

For this determination, which is carried out exactly as for the determination of silver in lead, large amounts of cadmium (of 100 mg. and more) already cause very distinct errors which may be as much as 20%. With amounts of cadmium over 100 mg., the transition point from yellow to pink appears much too soon. 50 mg. of cadmium on the other hand are still without effect on the transition point. Amounts of silver up to $10^{-3}\%$ can be determined with sufficient exactness.

e. The determination of silver in the presence of arsenic (152)

Can be carried out without difficulty since arsenic does not react with dithizon. Also in the titration of amounts of silver of the order of magnitude of 7.63×10^{-3}–$7.6 \times 10^{-5}\%$ one still obtains very good values.

f. The determination of silver in the presence of antimony (152)

Relative to this determination, that which was already said for the silver-arsenic separation holds good throughout. The determination of 1.86×10^{-2}–$1.9 \times 10^{-4}\%$ silver offers no difficulty.

g. The determination of silver in the presence of bismuth (152)

The determination is made possible through the fact that the orange red color of the bismuth dithizon complex in neutral solution is formed in weakly acid solutions only with relatively large amounts of bismuth (over 500 mg. Bi/10 ml.). For example, in the presence of 400 mg. Bi the change is first from yellow to olive green. This change is taken as the correct end point and the red orange color arising after the addition of 3–4 drops more is disregarded. Amounts of silver in the order of magnitude of 10^{-2}-$10^{-4}\%$, can still be determined with sufficient exactness.

h. The determination of silver in the presence of copper (152)

When both silver and copper are present, silver reacts with dithizon first—provided that the excess of copper is not too great. Qualitatively, silver in the presence of 100 times the amount of copper can still be distinctly recognized by the yellow color of the CCl_4 phase. With larger amounts of copper, a mixed color between yellow and violet appears with increasing content which makes the detection of silver uncertain.

For the quantitative determination (in the presence of 400 mg. Cu and 100γ Ag) a dark brown, mixed color appears at the start and not the pure yellow color of silver dithizonate. The end point is a color change to reddish brown which is rather difficult to detect. Since this transition appears too soon, the silver values are 10–20% too low. The same difficulties are encountered in the determination of 100γ Ag in the presence of about 50–300 mg. of Cu. Better agreeing results are obtained when the copper content is not greater than 1–5 mg. Then the yellow color of the silver dithizonate is still unchanged and the transition to reddish is more distinctly recognized. Also the end point for this ratio appears at the correct point. The exact determination of the transition point is, however, in spite of this, not wholly simple. One must shake especially well in the neighborhood of transition point, otherwise it is reached too soon. In spite of this defect, the determination of about 0.1–1% silver can be done with sufficient exactness.

Smaller amounts of silver in the presence of larger amounts of copper can, however, be determined in the following way. By shaking the silver dithizonate with potassium thiocyanide, the dithizonate is replaced with the formation of a complex silver thiocyanide. Since the copper dithizonate is not acted upon by the potassium thiocyanide, the silver compound can be extracted in this way from a mixture of both dithizonates.

Determination procedure: The silver and the copper are shaken out of a weak nitric acid solution in the usual manner. As already mentioned, the color from the beginning in the presence of larger amounts of copper (100 mg.) is not pure yellow, but somewhat brownish. At first the silver in the extract preponderates but by further shaking the copper content of the mixture increases and finally the pure color of the copper dithizonate arises. For complete separation of the silver therefore, it is necessary to shake until the pure violet color of the copper dithizonate appears. In this way one obtains the total silver together with very small amounts of copper in the carbon tetrachloride layer. This solution is first washed once with 1% sulfuric acid solution and then treated three times with a mixture of 5 ml. of 2% potassium cyanide solution and 1 ml. of a 1% sulfuric acid solution. The aqueous extracts separated from the carbon tetrachloride layer are combined and, after washing with pure carbon tetrachloride, evaporated. About 2–3 ml. of conc. sulfuric acid are added to the residue in a porcelain dish, the solution heated until SO_3 fumes are given off vigorously and then evaporated to dryness on the sand bath in order to destroy the complex thiocyanide. The thiocyanide free residue is now dissolved with 2 to 3 ml. of 2.5N nitric acid under gentle warming and diluted with water to 15–20 ml. In this solution, the silver is determined as already described.

Although the determination of smaller amounts of silver with this procedure is possible, the presence of about 250 mg. of copper always gives results which are considerably too low. Starting with about 100 mg. of copper, the results are satisfactory. Then silver quantities of the order of magnitude of about 0.001% can be determined.

j. The determination of silver in the presence of mercury (152)

Since mercury, similar to the silver, gives a somewhat darker yellow in acid solution with dithizon, a direct quantitative determination cannot be carried out. However, since mercury does not react with a weakly acid potassium thiocyanide solution to form a complex, silver can be determined in the presence of mercury. However, it is possible to treat only proportionately small amounts of mercury since larger amounts can be completely extracted with dithizon (152, p. 19) only with difficulty and by using disproportionately large amounts of dithizon solution.

Determination procedure: The solution of both metals is acidified with about 2.0 ml. of 2.5N nitric acid per 10 ml. of solution and then shaken with portions of the reagent solution until both metals are removed from the aqueous phase. Now the carbon tetrachloride layer is treated with 3–5 ml. of a 1% potassium thiocyanide solution and with 0.5–1 ml. of a 1% sulfuric acid solution in the same way as is described for the determination of silver in the presence of copper. The potassium thiocyanide extractions are evaporated, fumed with sulfuric acid and the evaporation residue taken up with 2.5N nitric acid. After sufficient dilution the silver is titrated in the usual way.

The exactness to be obtained from this procedure is somewhat less than by the former determination; however, the errors do not exceed the error limit allowable for micro analysis.

About 6–100γ silver in the presence of 100 mg. mercury gives sufficiently exact results.

k. The determination of silver in the presence of gold (152)

In the course of known procedures for the gold-silver separation, it is often of value to determine small amounts of silver in gold.

Determination procedure: The gold bead containing silver is fumed in a dish with conc. sulfuric acid on a sand bath. (The use of sulfuric acid is recommended because traces of silver, as is well known, are not completely dissolved out of gold with nitric acid.) Now the evaporation residue is heated a short time with several milliliters of 2.5N nitric acid, diluted with water and then allowed to stand on the water bath about 20 minutes. From the filtered solution the silver is determined in an aliquot part by titration with dithizon.

In this way, 100–12γ of silver can be satisfactorily determined in the presence of 10 mg. of gold. The error is between $+2.0$ and -2.9γ of silver.

l. The determination of mercury (153) (154)

Since the formation of mercury-dithizonate, especially with the last part of the mercury, takes place very slowly, its volumetric determination cannot be carried out with the exactness obtained in the silver determination. As a result of this slowness, the direct titration is unsatisfactory. Therefore, an indirect method was worked for the determination of mercury. The mercury solution is extracted with a measured excess of dithizon. The excess of dithizon is determined in an indirect way. The dithizon excess is replaced by a measured amount of a standard silver solution (likewise in excess) and the silver excess determined by titration with dithizon. Since the total dithizon used is known (a ml.) and by titration with silver solution, the amount of dithizon which does not enter into reaction (b ml.) is bound; one can from the difference—total dithizon (a ccm.) minus excess of dithizon (b ccm.)—calculate the amount of dithizon held by mercury (t ccm.). Since in acid solution 1 Hg combines with 2 mols. dithizon, by a simple calculation from the amount of dithizon entering into reaction (t ml.) the amount of mercury is determined.

Reagent solution: The solution, prepared as earlier described, should contain about 2–4 mg. dithizon per 100 ml. of silver solution. On account of the instability of silver solutions, a very dilute silver solution is prepared from a more concentrated solution (about 0.2-0.3 mg. Ag/ml.). For the standard, a measured volume of this solution is diluted about 20 times with chlorine free water. This solution keeps its titer around one to two days.

Titration procedure: The mercury solution is acidified with nitric or sulfuric acid until it is about 1N. The solution should contain about 0.5–5γ/ml. of mercury. A 10 ml. sample is used for the test.

First the mercury is removed from the acid solution by extracting with several portions of the standard reagent solution and shaking vigorously after each addition. The yellow CCl_4 layers are collected in a glass cylinder with a ground glass stopper and the extraction continued until the reagent solution remains a distinct green color. The total amount of dithizon solution used (a ml.) is then measured. (By using HCl or Cl^- ions, a small residue of Cl^- ions could remain in the CCl_4 layer and would, during the following addition of the silver solution, react with the silver. If Cl^- ions are present in the test solution then the CCl_4 layer must be shaken with dilute (1%) HNO_3 until the Cl' reaction is negative.) A determined volume of the dilute silver solution is now added to the Cl^- free dithizon solution and the solution shaken vigorously (1 part silver is added for 2.37 parts of dithizon). Since the main part of the dithizon is combined with mercury there is surely an excess of silver over the free dithizon. The silver excess is now back titrated with dithizon (b ml.).

A numerical example of the evaluation is presented below:

Silver titer of the dithizon solution..	6.02 γ Ag
(that is, 1 ml. of dithizon = 6.02 γ Ag, or 5.6 γ Hg.)	
Total reagent used.....	21.80 ml. (a)
Reagent solution corresponding to 74.4 γ Ag..	12.35 ml. (b)
Reagent solution corresponding to the Hg	9.45 ml. (t)
Mercury present = 9.45 × 5.6 = 52.9 γ Hg	

Relative to the determination of Hg in the presence of other metals, refer to the cited work of H. Fischer and G. Leopoldi (153).

m. The determination of zinc (155)

H. Fischer and G. Leopoldi recommend the following procedure for the quantitative determination of zinc: About 10–20 ml. of the zinc solution which should contain between 5–40γ of zinc is used for examination. The solution should be weakly acid (about 1–3% mineral acid, i.e. hydrochloric acid). A greater excess of acid is removed as nearly as possible by evaporation; neutralization with alkaline reagent is not recommended since traces of zinc can easily be introduced in this way. The solution is first tested for copper, mercury or the noble metals by shaking vigorously with several milliliters of the green dithizon solution. If the green color remains unchanged, then the solution is free from these metals. Should traces of these metals be present, they can be removed by extracting once or twice with the dithizon solution.

The carbon tetrachloride layer is carefully separated in a separatory funnel and washed with pure carbon tetrachloride. Now sodium acetate solution is added until blue congo paper changes to red and then half of the volume so far added poured into the funnel. The dithizon is removed by washing with 5 ml. of sodium sulfide solution (40 ml. of 1% solution to 1000 ml. of distilled water). Then the metal content is determined as usual.

In those cases where Cu, Ag, Hg (II), Pd, Au (III) are present, they are reduced with hypophosphorous acid to the corresponding metals. For a more detailed explanation the cited work of Fischer and Leopoldi must be consulted.

The same authors (156) also made purity tests with the dithizon procedure. It can be used to test for impurities in zinc and zinc alloys.

P. L. Hibbard (157) found that none of the methods for determining small amounts of zinc were very satisfactory and thus proposed the following method to determine zinc both in vegetable and animal substances.

1. **Preparation of the test solution:** Organic substances are removed by igniting to red heat and the ash extracted with dilute hydrochloric or sulfuric acid. If the ignition is difficult or if the ash formed melts easily, wetting with a little magnesium nitrate before the ashing helps. However, ignition in the wet way is not recommended since then zinc can easily be lost. Also the nitric or perchloric acid must be quantitatively removed, which is not always easy to do.

Small amounts of organic contamination can be removed with hydrogen peroxide, however, care must be taken in this case that the excess hydrogen peroxide be quantitatively destroyed. Slight organic contamination does not disturb the zinc determination with dithizon in many cases.

Salt solutions need no special procedures; in the presence of calcium, iron, phosphoric acid and other metals which precipitate in alkaline solution, ammonium citrate is added to prevent their precipitation.

In the analysis of alloys, a direct zinc determination is possible only when the alloy contains no component which may be precipitated with ammonia despite the addition of a "masking" agent.

2. **Special precautions:** There is considerable danger that the reagents will contain traces of zinc and thus introduce errors in the determination. In every case it is necessary to run a blank determination with every test. Thus the results can be corrected to true values.

A solution of 15 mg. of purified dithizon (see p. 119) in 100 ml. of chloroform is used as reagent solution. It is essential that the chloroform does not contain any oxidizing components. The presence of such substances is recognized by the fact that a concentrated dark green solution of dithizon is changed into a yellow color by dilution. The chloroform is purified by adding a little sodium thiosulfate solution and several drops of aqueous sodium hydroxide and distilling. The distillate is again distilled over a little sodium thiosulfate and this distillate freed from any co-distilled water by freezing. D. A. Biddle (158) purified the chloroform as follows: After removing the aqueous layer, the chloroform is shaken vigorously with 5–10 vol. % sulfuric acid until it is colorless, then treated with calcium oxide, distilled over the calcium oxide and 1–1.5 vol. % of absolute alcohol added to the distillate.

The distilled water is surely freed from any zinc by redistilling the water in a pyrex flask fitted with a good trap. It is of little advantage to extract the distilled water with dithizon.

Zinc free hydrochloric acid is best prepared by allowing concentrated c. p. hydrochloric acid to drop into concentrated c. p. sulfuric acid and taking up the hydrogen chloride formed in zinc free distilled water. Distillation of c. p. hydrochloric acid is not successful for this purpose.

The separatory funnel and the glass apparatus should not be glass which contains zinc. The stopper is wet only with water, never greased.

The very greatest care must be used that one does not come in contact with substances made from copper, zinc or brass. Just by handling a brass tap, sufficient zinc comes off on the fingers to make the results useless.

The dithizon solution is best stored in a reagent cylinder with a smooth, flat bottom; it must never be sealed with a rubber stopper.

The zinc is extracted from the test solution in the following way: The solution is poured into a sufficiently large separatory funnel and then ammonia added until the solution is alkaline. If a precipitate comes down it is dissolved by adding the necessary amount of hydrochloric acid, 1–2 ml. of ammonium citrate solution added, and the solution again made alkaline with ammonia. Now several drops of dithizon solution and 5 ml. of chloroform are added, then the mixture is shaken for several seconds (not too long! an emulsion can be formed!) and allowed to stand for 1 minute.

In the absence of zinc or other heavy metals, the chloroform layer remains green and the aqueous layer is brownish yellow (ammonium dithizonate); in the presence of large amounts of ammonium salts, the aqueous layer is only very slightly colored.

In the presence of zinc the chloroform layer is more or less of a strong red color depending on the zinc present. More portions of dithizon are added and the shaking continued until a dithizon excess is evident in the chloroform layer; the color of the layer changes to blue. The aqueous layer is then a yellow color unless there is too much ammonium salt in solution.

The color changes brought about by other metals are listed in the table on page 118.

The chloroform layer is now separated into another separatory funnel and the aqueous layer again shaken with chloroform and dithizon. The chloroform layer should remain green—especially since an excess of dithizon should be used in the first extraction. (The chloroform layer may at the very most have a very faint red tinge.)

The chloroform extract is purified and the excess dithizon removed by 2 or 3 extractions with 0.02N ammonia a total of 3 times the original volume. (Concentrated ammonia decomposes the zinc complex and thus produces too low results.) After allowing to settle each time the aqueous layer is drawn off and added to the water from the chloroform layer. 10–15 seconds shaking is usually sufficient. When the aqueous layer is colorless and the chloroform layer is red, the washing can be stopped. (In the presence of copper or other metals which react with dithizon, the color is naturally mixed.) By washing in this way practically no zinc is lost since the zinc complex is nearly insoluble in 0.02N ammonia. However, if the washing is continued for too long a time, the results are sometimes too low.

The determination of zinc in the chloroform extract: With small amounts of zinc (0–10γ Zn) the intensity of the red color is proportional to the zinc content. The colors of the concentrated solutions are difficult to compare; the use of a blue filter facilitates the comparison.

If the unknown solution is not completely clear, the standard solution is prepared in the same way and both solutions placed in reagent tubes with flat bottoms (similar to Nessler-cylinders) for comparison. Since the color intensity lessens with time, it is absolutely necessary to prepare a fresh standard solution each day. This solution must be divided into standards which contain 1, 2, 4, 6 and 10γ Zn in 10 ml.

For approximate determinations the color of the unknown can be compared to red cellophane which has been standardized against a solution of known zinc content. The red dye, Amaranth 107 of the National Aniline and Chemical Co., is also satisfactory for this purpose. Naturally, the comparison against an aqueous solution is not satisfactory because the difference in the density and refractive index of the chloroform solution is too great.

The titration with bromine has proven quite satisfactory. The titration is based on the fact that the red color of the zinc dithizon complex is destroyed by oxidizing substances. For the determination of 5–30γ Zn, a solution of bromine in carbon tetrachloride is prepared so that 1 ml. of solution is equivalent to 10γ Zn. The color of the bromine solution is about the same as the color obtained when 2 drops of methyl orange are placed in 50 ml. of an alkaline solution; its titer is very close to 0.001N. The bromine solution is standardized against a solution of known zinc content.

It is not possible to use a solution of bromine in chloroform since then the titer is very changeable.

Titration procedure: The chloroform solution of the zinc dithizonate is placed in a 60 ml. narrow-necked flask which has a glass stopper. The bromine is slowly added with steady shaking until the red color disappears. Since the end point is not very sharp, an excess of bromine is added, the solution allowed to stand 1 minute, then 1 ml. of 20% potassium iodide solution, some starch solution and 5 ml. of a 1% sodium bicarbonate solution added and the excess back titrated with 0.001N sodium thiosulfate.

This method gives good results for the determination of 3–30γ of Zn. With less than 3γ Zn, the colorimetric method is recommended.

Emulsions may be formed which make the determination very difficult. In this case, the extraction with dithizon is carried out, the dithizon excess washed out as completely as possible and then the emulsion allowed to flow slowly through a tube whose end is closed with a fine meshed bolting-cloth. This destroys the emulsion. The solution is now poured into a separatory funnel and the chloroform and aqueous layers separated.

Finely divided precipitates can not be removed by filtration because the filter paper always adsorbs zinc. In this case, the precipitate is effectively removed by centrifuging.

The extraction of zinc with dithizon is naturally influenced by all metals which are likewise extracted by dithizon in weakly alkaline solutions. The following table shows the effect of pH and of any reagents which may be added.

	pH of the Aqueous Solution	Elements Extracted by Dithizon
1	under 2	noble metals and Hg
2	2-3	Cu, Bi, Sn(II)
3	4-7	Zn, Cd, Pb, Tl and all metals of Group I and II
4	4-10	all metals of Group I-IV; washing with 0.04 N ammonia removes Sn(II); by adding KCN only Pb, Tl, Bi react
5	over 11	Cd is held; Zn is extracted

The announcement of H. Fischer (152), that zinc is quantitatively extracted from an acetate solution at a pH of 4, appears to be correct only when carbon tetrachloride is used. The separation of zinc from lead with carbon tetrachloride according to the method of Hibbard would probably be better, but by no means quantitative. With the use of chloroform as well as carbon tetrachloride, a partition equilibrium is set up which depends on the pH of the aqueous phase. The extraction of lead has already begun at a pH = 5 but is not complete until the pH = 7.

The influence of the pH on the extraction of 10γ Zn by a solution of dithizon in chloroform showed the following results:

pH	γ's Zn Extracted
3	0
4	1
5	4
6	7
7-10	10
11	2.5

It is therefore clear that zinc and lead cannot be separated at a determined pH value. However the separation is very simply done by adding some potassium thiocyanide.

Separation of zinc from lead: The solution is made alkaline with ammonia and extracted in the usual way with dithizon. After washing out the dithizon excess, the chloroform solution is shaken with 2 ml. of a 5% aqueous potassium thiocyanide solution and the layers separated. The chloroform layer which contains all the lead is washed with a little water and the wash water added to the thiocyanide layer.

This aqueous solution is evaporated in porcelain with hydrochloric acid (to destroy the thiocyanide) on the water bath and the residue moistened with 1-2 ml. of 1N hydrochloric acid. Sufficient water to cover the residue is added and the solution heated for several minutes. After cooling, the zinc is determined in the usual way with dithizon.

Separation of zinc from copper: The solution of both metals is extracted as a whole with dithizon and the excess dithizon removed with 0.02N ammonia. In this way copper and zinc are separated from iron and calcium.

The dithizon solution which contains all the zinc and copper is shaken with about 5 ml. of 0.5N hydrochloric acid and the chloroform layer transferred to a separatory funnel. The acid layer is washed with a little chloroform and the chloroform added to the dithizon solution in the separatory funnel. Now the chloroform layer is washed with 5 ml. of 0.5N hydrochloric acid and then added to the acid layer. The chloroform layer contains all the copper, the acid layer all the zinc. The excess dithizon is removed from the chloroform layer by washing with 0.02N ammonia. The metals can now be determined according to the usual procedures.

The method is not very exact since slight traces of zinc are held by the copper and slight traces of copper by the zinc. So far, a method which does not possess these errors has not been found.

If the test solution is free from Fe, Ca, etc., then a very exact separation of copper and zinc is possible:

The solution is adjusted to a pH of 3, then 2 ml. of 25% sodium acetate (pH = 3) added and the solution shaken 3–4 times with portions of dithizon solution. By treating the test solution in this way the zinc remains in the aqueous solution.

The exactness of the determination is about 5–10%—about the same order of exactness as the usual colorimetric method. The results of the bromine titration are also within 5–10% when 5–20γ of zinc are used.

n. Determination of cadmium (159): For determination of cadmium, the noble metals must be precipitated by reduction with hypophosphorous acid.

The extraction is carried out in alkaline solution (the final concentration is about 5% NaOH). The precipitation of hydroxides which would disturb the reaction is prevented by the addition of sodium tartrate or sodium citrate. The separated carbon tetrachloride extract is washed several times with 2% sodium hydroxide and finally with dilute acid. The green color is compared with a standard or an excess of silver added and titrated with dithizon (see p. 126). The analysis error is usually about 1–5%; for less than 5γ Cd, about 5–10%.

3. Colorimetric Determination

Basis of the method: The color of the metal dithizonate shaken out of the test solution is compared with the color of a similarly treated standard solution in a colorimeter. In some cases this comparison is not exact and the following gives better results: the dithizon is liberated from the metal dithizonate (in the free state) by acid and the green solution of the dithizon in CCl_4 colorimetrically measured against a solution of known dithizon content.

a. Determination of silver (*153*)

The colorimetric determination of silver is carried out in weak acid solution. The yellow silver dithizonate soluble in carbon tetrachloride is unaffected by dilute ammonia and therefore the slight excess of dithizon can be removed from the carbon tetrachloride solution by washing with very dilute ammonia.

Reagent solution: A solution, purified as usual, of about 6 mg. dithizon in 100 ml. purest carbon tetrachloride.

The dithizon excess is removed by washing with very dilute ammonia (1 volume of concentrated ammonia and 1000 volumes of purest distilled water). This wash solution should be practically free from heavy metals. Thus it is necessary to use double distilled water which was distilled the second time out of a glass flask.

Determination procedure: The nearly neutral solution containing silver (content about 1–12γ Ag/mg.) is acidified with about 2 ml. of dil. nitric acid (concentration about 15% by weight) for each 10 ml. The silver is now extracted in a separatory funnel with about 5 ml. of the green dithizon solution. One allows to stand a short time and then separates the now completely clear layers. The carbon tetrachloride layer is collected in a glass cylinder with a glass stopper. The aqueous layer is now shaken again with small portions of reagent solution until the green color of the reagent solution remains unchanged even on long shaking. For complete separation of the dithizon solution from the aqueous layer, the aqueous layer is rinsed with a small amount of purest carbon tetrachloride and the wash solution added to the silver dithizonate solution. The silver dithizonate in the glass cylinder is now shaken well with the dil. ammonia solution (1–1000) whereby the excess of dithizon passes into the aqueous phase. (In the presence of other metals it is shaken with dil. sulfuric acid before this in order to remove metals not reacting with dithizon in acid solution. This is necessary in the presence of Zn, which would also react in acid solution at higher concentration forming a red color.) The pure solution of silver dithizonate is separated and covered over with 1–2 ml. of 1% sulfuric acid to protect against premature evaporation of the CCl_4. In this way the solution can be kept in the dark without change for several days.

In the same way a comparison standard is prepared using a silver solution of known content.

Before the comparison, the sulfuric acid layers are separated from both solutions and carbon tetrachloride layers filtered through a dry folded filter. By this procedure, 12–111γ of silver can be determined with a maximum error of +4γ.

A standard curve plotted from known silver concentrations shows a straight line course; thus the changes of color intensity correspond to Beers law.

Under certain conditions the color tone of the standard and of the test solution may not match one another exactly; according to the experience of the authors this does not disturb the determination.

Colorimetric determination in presence of other metals: The determination is prevented by the presence of copper, gold, silver, palladium and platinum (II).

The presence of other elements, in general, is not disturbing (up to 1000 fold excess).

b. Determination of lead (160)

The determination depends on the extraction of lead with the green reagent solution. The reagent excess is removed from the lead dithizonate solution by washing with 1% KCN solution. Then by washing with mineral acids the red color changes into green. This green color is now measured colorimetrically.

Determination procedure: Dilute ammonia is added to the test solution whose lead content should lie between about 6–120γ. (In the presence of metals which are precipitated by ammonia, a sufficient amount of Rochelle salts is added to keep these metals in solution.) The lead is now extracted in the separatory funnel with about 5 ml. of reagent solution, the red dithizon solution transferred to a glass stoppered cylinder and the extraction repeated using small portions of reagent solution until the carbon tetrachloride layer is no longer colored red. The aqueous solution is washed with pure carbon tetrachloride to remove the last traces of dithizon and this solution added to the dithizon solution in the glass cylinder. This dithizon solution is washed once or twice with 1% KCN solution to remove the excess of dithizon. The free dithizon goes into the aqueous phase with a yellow color and when the washing is complete, the wash solution is colorless. Then the carbon tetrachloride layer is washed once with distilled water and separated from the wash solution. The aqueous layer remaining is rinsed with a little pure carbon tetrachloride. The lead dithizonate solution is poured into a measuring cylinder to a determined volume (10 or 20 ml.) and shaken with dilute hydrochloric acid (1:1). The red color is changed over into green. The green solution is filtered through a dry filter to remove the acid and then compared to a standard solution in the colorimeter.

(The decomposition of the red lead complex and the colorimetric comparison of the green dithizon solution is necessary because the red solution can not be measured with sufficient sharpness.)

The **comparison standard** is prepared from a standard lead solution (about 12γ Pb/ml.) in the same way. If the comparison solution is kept under sulfurous acid and in a dark bottle, it will keep very well for a long time; however, it is recommended to check the titer from time to time with a freshly prepared solution.

Lead can be determined in potassium cyanide solution in the presence of practically all metals. Oxidizing substances are rather disturbing in the presence of potassium cyanide since they color the carbon tetrachloride solution yellow to brownish during the shaking. They should be removed as completely as possible from the solution. If some traces are unavoidable, the determination can be successfully carried out in the presence of hydroxylamine hydrochloride (about 0.1-0.2 g. of the solid salt). Tin (II) and bismuth react similarly to lead. However, the lead can be determined in the presence of these metals without separating if they do not exceed the lead contents by more than 2 or 3 times.

The determination, in the presence of tin, is carried out exactly as described above—until the red color no longer is formed. If there is a large excess of tin, the solution is evaporated and fumed with a mixture of bromine and hydrobromic acid (d = 1.38) (Br_2:HBr = 1:4) on the water bath. The tin free residue is taken to dryness in the presence of several milliliters of aqua regia and then dissolved in 1–2 ml. of a 10% Rochelle salt solution. The solution to which potassium cyanide has been added can be measured colorimetrically.

In the presence of bismuth the solution must be shaken out until the appearance of the bismuth color (orange); since the lead is quantitatively extracted before the bismuth comes out, the lead can be completely removed.

The colored carbon tetrachloride solution is washed 3 or 4 times with 1% potassium cyanide solution until the aqueous phase comes through colorless and then it is washed with distilled water. The tin and the bismuth compound is decomposed by the potassium cyanide.

The procedure is also suitable for the determination of contaminants of lead in very small samples (0.1–0.5 g.) of alloys with very great exactness.

A slightly different lead determination has been described by O. B. Winter, H. M. Robinson, F. W. Lamb and E. J. Miller (161).

Wayne E. White (162) recommends the following procedure for the determination of lead left on fruits by lead sprays. The method depends on the fact that dithizon dissolves insoluble lead salts very well in the presence of potassium cyanide, ammonia and citric acid. Since the characteristic color reaction is not destroyed by the organic substances in the fruit peelings, the author recommends this method as a very suitable one.

A. W. Jewlanowa (163) determined lead in highly dilute solutions by using sets of colored glass and changing the procedure of H. Fischer in the following way: 10 ml. of the dilute lead solution are neutralized in a separatory funnel with ammonia and made alkaline with 0.5 ml. of dilute ammonia (1 part conc. ammonia to 200 parts water). 5 ml. of 1% potassium cyanide solution and 3 ml. of dithizon solution (6 mg. dithizon in 100 ml. carbon tetrachloride) are added to the ammoniacal solution and the solution thoroughly shaken. To prevent the precipitation of accompanying metals, at least 0.5 ml. of a 5% Rochelle salt solution is added. The colored dithizon solution is transferred to another separatory funnel and the aqueous solution treated with dithizon until no red color is formed. The last traces of dithizon solution are removed by shaking with 1 ml. of pure carbon tetrachloride. To remove the dithizon excess, the lead dithizonate solution is shaken with 5 ml. portions of 1% potassium cyanide solution until the aqueous solution is colorless and then the dithizon solution is washed with 40–50 ml. of double distilled water. The lead dithizon solution is transferred to a reagent cylinder with a ground glass stopper and diluted to 10 ml. The solution is compared to colored glass slides in the comparator (2 sets of glass; 0.0–1.0 mg. Pb/l and 1–10 mg. Pb/l).

L. Ellis (164) reports good use of the lead determination with dithizon in biological materials.

The enumeration and discussion of faultless results with dithizon procedures is naturally of especial interest because of the high sensitivity and specificity relations. H. Müller (165) has prepared a basic and critical investigation of the determination of lead with dithizon in biological substances. The author found from numerous pertinent experiments that excellent results with all biological materials could be obtained only if, before determining the lead,

1. the tin is removed by oxidizing,
2. oxidizing materials are entirely removed, and
3. bismuth is removed by shaking out in acid solution (pH = 2).

Since many extractions are necessary in the presence of large amounts of lead and since often it is necessary to remove large amounts of iron with hydrogen sulfide which is very difficult to wash out, Müller concluded that the dithizon method had no advantage over other methods.

More details, etc., must be referred to the original work.

c. *The determination of copper* (*160*)

Copper forms a brown color with dithizon in a neutral or alkaline solution and a violet color in acid solution. The reaction in acid solution is more sensitive since the violet keto compound, in comparison to the brown enol compound, contains double the quantity of dithizon. The determination is carried out as follows: The copper is shaken out of an acid solution freed from the reagent excess by washing with a very dilute ammonia solution. The pure violet color of the carbon tetrachloride solution is measured colorimetrically.

Reagent solution: The many times repeated directions are equally applicable to the strength and purity of this solution.

The **wash solution** is prepared by diluting 1 part of concentrated ammonia with 200 parts of double distilled water. If it should still contain minute traces of heavy metals, these can be removed by extraction with reagent solution (very little!).

Determination procedure: To the nearly neutral solution whose copper content is from about 4–50γ, about 2 ml. of 10% sulfuric acid is added for each 10 ml. of solution. The extraction with the reagent solution is continued as long as the violet color is formed from the green. For the shaking out of very small amounts of copper, continuous shaking (one to two minutes) is absolutely necessary. The reagent excess is removed by washing with the above-mentioned, dilute ammonia solution; one washes two or three times with 5 ml. of ammonia and afterwards washes the carbon tetrachloride layer once with sulfuric acid (1%). The solution is filtered through a dry filter, diluted to a determined volume and can now be colorimetrically measured.

The directions recommended for lead are applicable for this standard.

The determination can be carried out without previous separation for all metals with the exception of mercury, silver and gold. Large amounts of ferric salt are disturbing because of their oxidizing action and should be removed beforehand by some suitable method (perhaps by extracting $FeCl_3$ with ether).

The determination of copper in the presence of mercury can, according to H. Fischer and G. Leopoldi (160), be carried out without removal of the mercury by changing the mercury over into the iodide complex in which form it does not react with the dithizon.

The determination according to these authors is carried out as follows: About 2 ml. of a freshly prepared 5% potassium iodide solution are added to 10 ml. of the weakly acid solution containing mercury and copper. Now, the usual dithizon extraction is carried out and the separated dithizonate solution washed twice with 1% sulfuric acid then 2 or 3 times with dilute ammonia (1:200). Since larger amounts of potassium iodide influence the formation of the copper dithizonate, the determination can only be carried out with small amounts of mercury (under 1.5 mg.) which do not need too great an excess of KI to form a complex.

d. The determination of mercury (153)

Hg (II) salts react in strong acid solutions with dithizon, always forming the orange colored dithizonate, Hg_2D (D = dithizon molecule). This dithizonate is stable in dilute ammonia solution. However, during washing with ammonia, the dithizon forms a dissociable ammonium salt yellow in color in the aqueous phase which may make separation of the layers somewhat difficult. As a result of the relatively great instability of the mercury complex, especially in the presence of a dithizon excess, one must wash quickly with ammonia and also carry out the colorimetric determination very quickly. These unfavorable characteristics made it appear more suitable to evaluate the green color of the pure dithizon instead of the orange colored complex. The mercury dithizonate cannot be decomposed by acid but immediately decomposes in the presence of KI.

As **reagent solution,** a solution of about 6 mg. dithizon and 100 ml. CCl_4 is used.

For the removal of the reagent excess, a very dilute ammonia solution is used (one part concentrated ammonia diluted with 1000 parts of water).

Determination procedure: 10–20 ml. of the test solution (0.5–5γ Hg/ml.) are placed in a separatory funnel, the acidity adjusted to 1N and the mercury shaken out with about 5 ml. of the green reagent solution. After the funnel has stood for $\frac{1}{2}$–1 minute, the CCl_4 layer is separated from the aqueous layer and the dithizonate solution collected in a glass stoppered cylinder. The aqueous solution is now completely extracted with small portions of reagent solution. The extraction is finished when the reagent solution retains its green color despite vigorous shaking. The dithizonate solution, collected in the glass cylinder, is now shaken twice in a separatory funnel with 5 ml. portions of the dilute ammonia solution. (In carrying out the determination in the presence of other metals, previous washing with dilute H_2SO_4 is necessary.) The purified mercury dithizonate solution is now washed twice with a weakly acid (H_2SO_4) 1% KI solution whereby the orange immediately changes to green. The free iodides present in the carbon tetrachloride solution are removed by washing with water and with a very dilute solution of sulfurous acid. The sulfurous acids prevent oxidation of the green dithizon solution, which would otherwise occur after a short time.

The comparison solution is prepared in the same way. Freshly prepared (daily) solutions give the best results since very dilute mercury solutions may change their titer within a few hours. Therefore a concentrated solution (about 0.3 mg. Hg per ml.) is used as standard and an aliquot portion diluted to a suitable mercury content for the actual comparison solution.

The values announced show good agreement.

The colorimetric determination of mercury in the presence of other metals is described in the cited publication (153).

The colorimetric determination can be carried out from still another basis, which depends on the comparison of determined mixed colors. This method is based on the fact that the ion to be determined is shaken (perhaps) with a solution of a metal dithizonate (i.e. silver with a copper dithizonate solution) and the mixed color appearing measured colorimetrically. Also the mercury can be shaken out with the green dithizon solution and the mixed color resulting from this excess of dithizon measured colorimetrically. This procedure is suitable for determining very small amounts of metal from about 0.1–2γ.

H. Grubitsch and J. Sinigoj (166) have recently studied the errors of the mixed color determination, particularly with reference to the determination of copper and zinc. The scope of this book does not allow a detailed discussion of their findings. Therefore it is advisable to consult the original work.

The exact determination procedure for silver can be found in (152, p. 20) and for mercury in (153, p. 249).

The varied use of dithizon is apparent from the numerous publications. However there is naturally not enough room in this work to consider all these methods and uses. H. Fischer (167) has published a monograph which covers a great deal of the work, particularly that done recently.

E. B. Sandell (168) has recommended dithizon for the determination of lead, copper and zinc in silicate rocks.

N. L. Allport and G. H. Skrimshire (169) have published a work on the determination of lead in nutrients and biological materials. J. Gangl and E. Liedl (170) determined lead in milk. Recently K. Heller and coworkers (171) have applied the use of dithizon to the detection of heavy metals in mineral waters.

F. Rohner (172) has used dithizon as an aid in spectral analysis.

XIII. Sulfosalicylic Acid (35), (36), (37)

The commercial sulfosalicylic acid is best purified in the following manner: A saturated solution of the acid is prepared in 96% alcohol at room temperature, allowed to stand for some time (several days) and then the residue, which consists mainly of calcium sulphate, filtered off. By repeating this operation 2 or 3 times, all but minute traces of inorganic contamination are removed.

Since the purest preparation that can be bought contains inorganic contaminations, the preparation of sulfosalicylic acid is described here. By using doubly sublimated salicylic acid and purest sulfuric acid it appears possible to obtain a product that is completely free from impurities.

Preparation of sulfosalicylic acid: Enough purest concentrated sulfuric acid is added to 50 g. purest salicylic acid in a 300 ml. beaker to form a mushy mass. This is then heated on a sand bath whereby sulfonation occurs (with a slight excess of H_2SO_4 the mass sometimes becomes completely solid). The heating on the sand bath is continued until the mush becomes fluid and the color is changed over from a dark orange to violet brown. The product is now allowed to cool with constant stirring in order to avoid forming a solid mass and the cooled product dissolved by slowly adding water. For analytical purposes, preparation of the pure acid in the solid form is not necessary. Therefore the aqueous solution is neutralized with ammonia to a color change into yellow-green, the neutral solution just acidified with several drops of 2N sulfuric acid and this solution diluted to 500 ml. The ammonium sulphate present does not interfere in the use of the reagent.

If one begins with the commercial sulfosalicylic acid which has a maximum ash content of 0.1%, then it is not recommended to purify the acid as the lead salt. A product which contains only 0.05% ash is obtained; however, lead is introduced and cannot be removed by many recrystallizations. Since the commercial acids contain only traces of iron and somewhat more calcium and magnesium, it is recommended to determine the ash content of the reagent and to make corrections in the evaluation of the results. Since the acid forms soluble complexes which are important because of their reactions with other reagents, the reagent is practically always used to accomplish separations.

1. Separation of Titanium from Iron (35)

This separation is based on the fact that although both iron and titanium form complexes with sulfosalicylic acid, the pH is adjusted so that the iron may be precipitated with H_2S. (Compare also to (97).) Moreover compared to the usual reagent, tartaric acid, sulfosalicylic acid has the advantage that it can be easily removed by evaporating the filtrate and sublimating off the acid at low temperature (280°).

Separation procedure: The oxide mixture is fused with potassium bisulfate or with sodium carbonate, the melt dissolved in cold dilute sulfuric acid and then 50 ml. sulfosalicylic acid solution (3 g. acid in 200 ml. of water) added to the solution. Ammonium carbonate is added to the opaque, violet-black solution until the color is changed to a clear red. (The solution is now adjusted to a pH value corresponding to the free phenol groups.) The solution is diluted to 200 ml., H_2S passed in the cold solution for one half hour and the FeS filtered off. (A little filter pulp facilitates the filtration.) Since $Fe(OH)_3$ which could be formed by oxidation of the air is soluble in sulfosalicylic acid containing H_2S (35, p. 662) the filter must always be filled to the edge. Also the ferrous sulfide is washed until the filtrate comes through completely colorless. The wash water is prepared by mixing 10 ml. of the sulfosalicylic acid with 200 ml. of water, neutralizing this mixture exactly with the ammonium carbonate and passing H_2S into this solution until it is saturated. Now this wash solution is replaced by washing with water saturated with H_2S until the filtrate no longer gives a violet color when tested with weakly acid ferric chloride solution. The ferrous sulfide is now transposed to Fe_2O_3 by ignition.

The filtrate is supersaturated with ammonia, and the titanium precipitated by boiling for about five minutes.* The precipitate is allowed to settle, decanted several times with hot, ammoniacal water, filtered and finally ignited half an hour over the blast lamp.

2. Separation of Titanium from Aluminum

Basis of separation: The titanium (IV) sulfosalicylicate complex is decomposed in ammoniacal solution through boiling and titanic acid precipitates while the aluminum compound remains in solution. However the precipitate always contains aluminum as a result of adsorption. Since the precipitated acid is soluble in strong hydrochloric acid (35, p. 682) and soluble in sulfosalicylic acid, the aluminum can be practically eliminated by double precipitation.

Procedure: 50 ml. of sulfosalicylic acid solution (concentration as above) are added to the hydrochloric or sulfuric acid solution of both salts, then the solution made strongly alkaline with ammonia and boiled five minutes over a small flame; the precipitate settles quickly. The clear solution is filtered hot and the precipitate decanted twice with hot, ammoniacal water. In order to dissolve the precipitate 50 ml. of concentrated hydrochloric acid and the same volume of sulfosalicylic acid (compare to footnote) are added and the solution allowed to stand ten minutes on the water bath. After this dilute ammonia is added dropwise with cooling until a clear yellow solution (complex ion of Ti (IV)) arises. Then the solution is supersaturated again with ammonia,† boiled five minutes, filtered after the settling and washed with hot ammoniacal water. The still wet filter is ashed and ignited half an hour over the blast.

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* According to a private communication from A. Brukl, a larger excess of sulfosalicylic acid prevents quantitative precipitation. By using about 0.3 g. of the oxide mixture, there is always sufficient sulfosalicylic acid present to keep the aluminum in solution.

† It does not appear justified to suppose that the considerable ammonia which is used caused SiO_2 errors.

If, in the mineral analysis, the sum of the oxides ($Al_2O_3 + TiO_2$) was determined, then the determination of aluminum by difference is generally sufficient. If, however, it is necessary to determine the aluminum alone, the filtrate from the titanium precipitate is evaporated to dryness in a porcelain dish and the residue heated to 280°. Thereby the sulfosalicylic acid is quantitatively sublimated (under partial decomposition into salicylic acid and sulfuric acid). The residue is dissolved in warm concentrated hydrochloric acid and a spot test with a micro drop of ferric chloride made in order to show the absence of sulfosalicylic acid. If this showed the complete removal of the acid, then the aluminum is determined according to one of the well-known methods.

3. Separation of Titanium from Iron and Aluminum

By combination of the above described separations, the separation of titanium from iron and aluminum can also be carried through. Since the individual determinations are done exactly according to the above announced directions, it suffices here, to sketch briefly the analytical procedure:

a. Determination of the sum of the oxides $Fe_2O_3 + Al_2O_3 + TiO_2$.

b. Fusion of the oxides with potassium bisulfate; precipitation of the sulfuric acid solution after adding sulfosalicylic acid and neutralizing the ammonium carbonate by passing in H_2S.

c. The ferrous sulfide filtrate is supersaturated with ammonia and kept gently boiling five minutes; the further treatment takes place as in the separation of titanium from aluminum.

d. The determination of aluminum is most simply calculated from the difference.

If the results obtained by this method do not check exactly with the amounts used, the errors do not, by any means, exceed the allowable limits.

4. Separation of Iron from Manganese

The method depends on the fact that iron forms a complex salt with sulfosalicylic acid in ammonia solutions, but not manganese. In the presence of sufficient sulfosalicylic acid iron is not precipitated by ammonium phosphate while manganese is quantitatively precipitated as $Mn(NH_4)PO_4$.

Separation procedure: 15 to 20 g. of solid ammonium chloride and 50 ml. of the reagent solution (330 g. sulfosalicylic acid per liter (37, p. 382)) are added to the solution of ferric and manganese chlorides for each 0.5 g. of oxides. Sodium phosphate and ammonia drop by drop is now added with stirring until the reaction is weakly alkaline. A larger excess of ammonia is to be avoided because of the solubility of the precipitate (37, p. 382)! The solution is heated almost to boiling and kept warm until the precipitate is changed into the familiar gleaming crystals. After standing two hours on the water bath the precipitate is filtered through a filter crucible, washed with water containing ammonium nitrate until the chloride action disappears and then converted into the pyrophosphate by ignition in the electric furnace.

The iron is precipitated by passing H_2S into the filtrate and the FeS washed with water containing ammonium sulfide until the reagent is completely removed. The precipitate is dissolved in hydrochloric acid, oxidized with several drops of nitric acid and the iron precipitated with ammonia (37, p. 382).

The results obtained by this method are satisfactory.

5. Separation of Iron from Aluminum and Manganese

Out of a solution of the three metals to which the reagent is added, the iron and manganese are precipitated by H_2S in the way described for the separation of iron from titanium. Aluminum is precipitated from the filtrate according to the method described on page 143.

The sulfides of iron and manganese are dissolved and the manganese precipitated from this solution as $Mn(NH_4)PO_4$, according to p. 144.

6. Separation of Iron from Aluminum and Magnesium

Out of a solution of the three metals only the magnesium is precipitated in the presence of sufficient sulfosalicylic acid by sodium phosphate as $Mg(NH_4)PO_4$.

Separation procedure: 50 ml. of the reagent solution (330 g. sulfosalicylic acid per liter) and five to ten grams ammonium chloride for each 100 ml. are added to the solution (chloride, nitrate or sulfate) for an oxide content of 0.5 g. Now an excess of concentrated ammonia is added (solution must distinctly smell of it—better determined by an indicator), the solution heated to boiling and the magnesium precipitated with a 10% solution of sodium phosphate which one adds altogether under stirring. After the precipitation the solution is boiled several minutes under continuous stirring and finally concentrated ammonia added until the original volume is one-third larger.

After standing several hours in the cold the clear liquid is filtered through a filter crucible and the precipitate washed by decanting with a 3% ammonia solution containing 2 ml. of sulfosalicylic acid solution per 100 ml. of solution. The precipitate is transferred to the filter with 2½% ammonia and washed until completely free from sulfosalicylic acid (spot test with $FeCl_3$). If the $Mg_2P_2O_7$ obtained by ignition is not pure white, then the sulfosalicylic acid has not been completely washed out. By repeating the ignition and wetting the residue with two to three drops of concentrated nitric acid, the pure white product is obtained (173) (174).

The results obtained are good—especially in the presence of much aluminum and little magnesium (Al:Mg—10:1). This is of considerable value in the investigation of certain alloys.

7. *Codetermination of Iron, Aluminum and Phosphoric Acid, without Separating the Phosphoric Acid*

As is readily apparent, the method described here offers the possibility of determining phosphoric acid in the presence of iron and aluminum without previous separations.

Separation procedure: 50 ml. of sulfosalicylic acid (330 g. per liter)* for each 0.5 g. of oxide and 5–10 g. of ammonium chloride for each 100 ml. of solution are added to the solution which contains Fe, Al, H_3PO_4. Concentrated ammonia is added in slight excess, the solution heated to boiling and precipitated with stirring by adding a magnesia mixture all at once. The precipitate must be crystalline. If it should precipitate flocculently then there was either too little sulfosalicylic acid or too little ammonium chloride in solution. After the precipitation is finished, concentrated ammonia is added until the volume is increased one-third and the precipitate allowed to stand several hours in the cold. The $Mg(NH_4)PO_4$ is treated exactly as was described above. The other metals in the filtrate can be determined according to the already announced directions.

Since the determination procedure is very simple and the values agree well, the thought occurs to replace the citrate method by the above method. This is, however, not possible since calcium does not form a soluble complex salt and therefore would be precipitated with H_3PO_4.

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* According to A. Brukl (private communication to Dr. Boettjer) this high concentration is necessary since sulfosalicylic acid does not have such a strong ability to form stable complexes as tartaric acid. However, a greater excess of sulfosalicylic acid is not necessary in the presence of tartaric acid.

8. The Separation of Thallium from Lead (175)

Thallium (I) forms a soluble complex salt with sulfosalicylic acid which is not precipitated by ammonium phosphate.

Separation procedure: Several drops of sulfurous acid are added to the acid solution of both metals to reduce any Tl (III) ions present. The excess of sulfurous acid is removed by boiling and then 20 ml. of sulfosalicylic acid (1:2) (175, p. 714) added to the solution. Ammonium phosphate is added in excess, then the solution made weakly ammoniacal and heated to boiling for several minutes until the precipitate has become crystalline. The precipitate, $Pb_3(PO_4)_2$, is filtered after standing several hours, washed with water, which contains some ammonium nitrate and about 1% ammonia, and finally ignited in the electric crucible oven.

9. Separation of Thallium from Manganese (175)

After adding several drops of sulfurous acid, 20 ml. sulfosalicylic acid is added to the halogen free solution of both metals and the solution heated to boiling. 10% ammonium phosphate is now added and the solution kept at a temperature near boiling until the manganese precipitate gleams like silk. After the precipitate settles completely it is filtered through a filter crucible, washed with weakly ammoniacal water containing ammonium nitrate, ignited and weighed as $Mn_2P_2O_7$.

The manganese precipitate is free from thallium in one precipitation.

10. Separation of Thallium from Aluminum

Since aluminum forms a very stable, easily soluble complex with sulfosalicylic acid, thallium can be precipitated directly as the chromate (compare to page 148).

11. Separation of Thallium from Iron (175)

10 ml. sulfosalicylic acid for each 0.1 g. Fe_2O_3 are added to the solution of both metals and the solution heated to boiling. The solution is made ammoniacal and thallium precipitated out of the clear red solution as the chromate.

The separation gives good results using only one precipitation for all concentrations of thallium.

12. Separation of Thallium from Chromium (III) (175)

This is done in the same way, only the chromium determination in the filtrate is impossible. (According to the check analysis existing, the possibility of forming chromium (III) chromate under these conditions does not arise.)

13. Separation of Thallium from Mercury (175)

If sodium thiosulfate is added to an ammoniacal solution containing Tl (I) and Hg (II) salts, then both elements form difficultly soluble compounds. If, however, one adds sulfosalicylic acid beforehand then the soluble $Tl_2S_2O_3 \cdot Na_2S_2O_3$ as well as a soluble salt of mercury is formed. In this case only thallium is precipitated by potassium chromate.

Separation procedure: 1–2 g. sulfosalicylic acid is added to the solution of both metals for each 0.1 g. mercury and the solution made ammoniacal during which the solution must remain completely clear (otherwise too little sulfosalicylic acid has been added). Now 2 g. of sodium thiosulfate are added, any precipitation dissolved by gentle warming (at the most to 30–35°) and diluting with water and the thallium precipitated in the cold with potassium chromate and stirring. Considerable sodium thiosulfate is added to the filtrate, then it is strongly acidified and boiled, whereby HgS, mixed with much sulfur, precipitates. This precipitate is dissolved in sodium sulfide, any precipitated $Cr(OH)_3$ filtered off and the mercuric sulfide in the $Hg(SNa)_2$ solution determined according to Volhard (176). (Under these circumstances the HgS can be kept in the red form.)

In addition to this procedure, the determination of thallium as $TlCrO_4$ (175) is given:

The ammoniacal solution of the thallium (I) is heated to boiling and enough potassium chromate added under stirring to form an approximately 2% solution. After standing about 12 hours (very little thallium precipitates until the solution has stood a long time) the yellow precipitate formed is washed with 1% potassium chromate solution by decantation and finally filtered with 50% alcohol through a glass or porcelain filter crucible and washed until the liquid filtering through is completely colorless. The washing must be very carefully done in order to remove all adsorbed potassium chromate with certainty. The precipitate is dried at 120°.

C. PENETRATION COMPOUNDS AS DETERMINATION FORMS

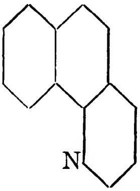
I. Napthoquinoline, "Naphthin"

M.W. = 179.0

M.P.(α) = 52°

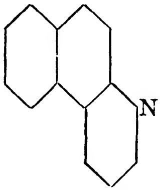
M.P.(β) = 93.5

$C_{13}H_9N$



α

or



β

The reagent forms precipitates in strong mineral acid solution with the following ions (39): Hg, Bi, Cu, Cd, Zn, U, Fe(III) (for constitution see 39, p. 27). The stability and insolubility increase in the following order: Cl, Br, I, SCN.

In the presence of Cl ions only Hg and Bi are precipitated.

In solutions containing Br or I, Hg, Bi and Cd precipitate. In the presence of H_2SO_4 or HNO_3, U and Fe(III) are precipitated as difficultly soluble thiocyanides of naphthin.

INDIVIDUAL DETERMINATIONS

1. Cadmium (39)

The first mentioned Cd-HI-Naphthin complex of the formula $(C_{13}H_9N)_2H_2CdI_4$ is insoluble in sulfuric and nitric acid but easily soluble in hydrochloric acid. It is decomposed by bases; organic solvents such as acetone and pyridine dissolve the compound easily; the compound is difficultly soluble to insoluble in alcohol, ether and benzol. Heating to 130° is possible without any decomposition. The sensitivity of the reaction (1:532,000) is noticeably lessened by Cl ions (1:355,000).

The solubility of the cadmium compound is small enough so that one part of Cd can be precipitated in 560,000 parts of dilute sulfuric acid.

Determination procedure: 50 ml. 2N sulfuric acid and 50 ml. of a 10% sodium tartrate solution are added to the cadmium salt dissolved in 0.3N sulfuric acid. The presence of tartrate ions have no effect on the cadmium precipitation; this is of importance for the separation of cadmium from easily hydrolyzable metals. Now a sufficient amount of 2.5% solution of the naphthin in 0.5N H_2SO_4* and several drops of a dilute solution of sulfurous acid are added to the solution. (The sulfurous acid is added to prevent oxidation or resination of the precipitant.) Now the cadmium is precipitated by adding sufficient 0.2N potassium iodide solution; the total volume should be about 150 ml. After 15–20 minutes the precipitate is filtered through a filter crucible and after sucking dry, is washed with a solution of the following composition: 10 ml. of a 2.5% reagent solution is diluted to 90 ml. with distilled water and 10 ml. of 0.2N potassium iodide solution added to it. The cadmium compound is practically insoluble in this solution. Care is taken that during the 1st, 2nd and 3rd washing, 2–3 ml. more of 0.2N potassium iodide solution is added to remove the greater part of the acid which is still present in the precipitate. The insolubility of the cadmium compound depends only on the acid concentration present in the precipitating liquid.

The precipitate is again sucked as dry as possible and decomposed by the addition of 20 ml. of 2N sodium hydroxide. Then it is acidified with sulfuric or hydrochloric acid and brought to an approximately 5% acid concentration. The solution is now titrated either according to the cyanide method of Lang or according to the iodine-acetone method of Berg with 0.1N potassium iodate solution.

1 ml. 0.1N KIO_3. . . . . .0.9366 mg. Cd.

a. Cyanide method (*177*) (*178*): Iodine is quantitatively changed into ICN by mineral acid solutions in the presence of strong oxidizing agents such as NO_2', MnO_4'', BO_3', IO_3', IO_4''.

$$I_2 + HCN \rightleftarrows ICN + H^+ + I' \qquad (1)$$

The iodine ion reacts in the presence of oxidizing substance according to the equation

$$I' = I + (e) \qquad (2)$$

while the equilibrium, according to (1), is pushed from left to right. Therefore, both reactions of which one is dependent upon the preceding one, are continued until finally all the iodine is oxidized to ICN. By combining (1) and (2), one obtains the following equation:

$$I + HCN = ICN + H + (e) \qquad (3)$$

---

* 2.5 g. of naphthin are dissolved in a mixture of 1.3 ml. of concentrated H_2SO_4 + 3 ml. of water and this solution diluted to 100 ml. with water.

for the oxidation of I to ICN. Iodide can, of course, also be oxidized to ICN according to:

$$I' + HCN = ICN + H^+ + 2(e) \qquad (4)$$

Therefore, this reaction can be used for the volumetric determination of iodine and iodide because the discharging of the I in mineral acid solution by IO_3 (and MnO_4) takes place very quickly and the endpoint of the oxidation can be recognized in the presence of hydrochloric acid with great sharpness by the disappearance of the iodine-starch reaction.

IO_3' reacts, as is well known, according to the equation,

$$IO_3' + 6H^+ + 5(e) = I + 3H_2O \qquad (5)$$

if the value from (3) is substituted for I,

$$I = ICN + H^+ + (e) - HCN,$$

then one obtains the general scheme for the oxidation effect of IO_3 in the presence of HCN.

$$IO_3' + HCN + 5H^+ + 4(e) = ICN + 3H_2O \qquad (6)$$

The titration is carried out according to the following directions: The solution of the iodide is acidified with the same volume (which should be at least 50 ml.) of 2–5N hydrochloric or 4–5N sulfuric acid and 6–8 ml. of 0.5N potassium cyanide solution and some starch solution added to it. One titrates now with 1/40 m. potassium iodate solution until the blue color just disappears.

The method can be used in the presence of bromide, chloride and nitrate.

b. *Iodine-acetate method* (*178, p. 69*) (*179*) (*180*)*:* This method depends on the oxidation of HCl, HBr and HI with $HBrO_3$ in the presence of acetone:

$$HBrO_3 + 2HI + 3C_3H_6O = 2C_3H_5O \cdot I + C_3H_5O \cdot Br + 3H_2O$$

for the oxidation by hydrogen iodide with hydroiodic acid.

The equation for this procedure is then:

$$HIO_3 + 2H\dot{I} + 3CH_3COCH_3 = 3CH_3COCH_2I + 3H_2O$$

The end of the reaction is recognized by the disappearance of the iodine-starch reaction.

Titration procedure: The iodide solution is diluted to a 50–60 ml. volume with water and, after the addition of 20–30 ml. of acetone, the acid concentration adjusted to 2–2.5N with a 50% sulfuric acid solution. The total volume should be about 100 ml. Then a little starch solution is added and the solution titrated with 0.1N KIO_3 solution. The rapidity of the titration must be so regulated that the iodine-starch color, which tends to be a dirty brownish color as a result of the transitory production of subiodic acid, keeps its normal blue color. In this way the approach of the endpoint of the titration is shown. Every drop of KIO_3 solution then added causes an always quicker fading of the blue color and when it completely disappears, indicates the end of the titration.

According to this procedure the **separation of cadmium from zinc** can be carried out without difficulty. Therefore, this method is especially valuable because it allows cadmium to be determined with satisfactory results in the presence of about 120 times as much zinc.

Also the separation of zinc from the metals of the $(NH_4)_2S$ group can be carried through smoothly according to the above directions in the presence of a tenfold excess of the other metals.

Separation of cadmium from antimony and zinc: The separation is carried out in a solution which is about 2N in acid concentration. The precipitation takes place according to the already announced method only a double amount of sodium tartrate or sodium oxalate is added to prevent hydrolysis. The cadmium is precipitated with a 10% potassium iodide solution and the filtered precipitate washed with a solution of the following composition: 50 ml. 2N sulfuric acid, 50 ml. 10% sodium tartrate, 20 ml. potassium tartrate solution and 20 ml. 0.2N potassium iodide solution are added to 10 ml. of reagent solution. Finally the precipitate is washed with the same solution used for the cadmium determination and then the cadmium determined by titration with KIO_3.

2. *Determination of Bismuth*

F. Hecht and R. Reissner (181) sought to work out a procedure for this determination which would serve for the separation of cadmium from the other metals of the H_2S group. Since this goal appeared possible only through "masking" of the companion metals (Cu, Sb and Sn) the determination was carried out from the very beginning in the presence of tartaric acid. According to the results of these authors, the bismuth precipitate is always contaminated with naphthoquinoline tartrate. Though it was possible to obtain correct results by using the right amount of the wash water, the precipitate was not formula pure. The traces of impurities present have been compensated for by traces of precipitate already gone into solution. The precipitation of bismuth with naphthin is quantitative in every case so that the determination gives usable results in the hands of a skilled analyst. Since the determination is the first practical example of a gravimetric determination with naphthin, the precipitation procedure worked out by Hecht and Reissner is given below.

α-naphthin was used by the authors. As already announced by Berg, the naphthoquinolines are the same in their action on metal salts.

Determination procedure: The volume of the bismuth salt solution should be measured so that after addition of all the precipitant the end volume for 10 mg. of bismuth is about 30 ml. The bismuth should be present as the sulfate and the solution should contain 3% free sulfuric acid. Solutions which contain other volatile acids or which do not have this acid concentration are evaporated to dryness, taken up with the corresponding amount of H_2SO_4, heated to evolution of SO_3-fumes and after cooling taken up with the corresponding amount of water. To the solution so obtained, 3–3.5 ml. of 2.5% naphthin solution* are added for each 10 mg. Bi, then about 0.5 ml. of a 10% solution of sulfurous acid and the solution heated until boiling begins. With the flame low 5–6 ml. of 0.2N potassium iodide solution are added dropwise and then the heat increased until the solution boils vigorously. After allowing to cool to room temperature, the cold solution is filtered through a porcelain filter crucible A_1† and washed twice using 3 ml. of the following wash solution for each 10 mg. Bi: 10 ml. of reagent solution are diluted with water to 100 ml. After strong suction of the wash solution the precipitate is washed with 5–6 ml. of cold water divided in several portions for each 10 mg. Bi. During this washing the precipitate should be stirred several times with a thin glass rod. The crucible is now sucked air dry in the apparatus described on page 44 and after completing the drying, the crucible is wiped first with a wet then with a dry piece of buckskin and after standing about one hour, is weighed in the balance. (Of course the crucible should be put in a desiccator before weighing.)

As already mentioned, the results which are obtained from this method are satisfactory throughout although not the formula pure compound is weighed.

The method can be used with practically no important changes as a semi-micro method. For 2–14 mg. of Bi_2O_3 the volume should be about 20 ml. regardless of the bismuth content. In washing the precipitate with water, about 1.5–2 ml. of water for each 2 mg. Bi_2O_3 is used.

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* 2.5 g. α-naphthin are dissolved in a mixture of 1.3 ml. of concentrated H_2SO_4 + 3 ml. of water and the solution diluted to 100 ml. with water.

† If a crucible of a greater porosity is used, some of the fine precipitate would

It must be pointed out here that the method only gives agreeing results when the precipitation directions are very exactly adhered to; this is true for any compensation method.

II. Thiourea

1. *The Determination of Lead* (*47*)

By saturating lead salt solutions which are acid and which contain nitrates with thiourea, practically insoluble thiourea nitrate, $2Pb(NO_3)_2 \cdot 11CS(NH_2)_2$, is formed. Almost all other metals form soluble thiourea complexes or soluble nitrates and remain in solution. If the lead precipitate is dissolved in hot water, then the lead can be precipitated as the chromate, anthranilate or picrolonate.

Ag, Hg, Cu, Bi, Cd, As, Sb, Sn, Co, Ni, Fe, Mn, Al, Cr, Zn, and Ba do not interfere. Thallium, however, reacts similar to lead.

The method is also of special advantage for the analysis of alloys. The other metal ions in the filtrate can be precipitated with hydrogen sulfide. Only copper is not completely removed in this way. However it can be determined in another portion of the solution with a special reagent (benzoin oxime, salicylaldoxime).

Determination procedure: The nitric acid solution of the sample is diluted with water until it is 1–2N with respect to the acid concentration. The total volume should not be too great since then large amounts of thiourea are needed. An equal volume of freshly prepared thiourea solution (the solution is about 1N with respect to nitric acid and is saturated at 25–30°) is added to the solution, or if the volume of the solution is sufficient, solid thiourea may be added to the solution. The solution is now cooled thoroughly by placing in ice water. The precipitate comes down in small white crystals in a needlelike form. In the presence of silver or considerable copper a crystalline precipitate is formed when thiourea is first added but this dissolves with the addition of more thiourea. A little more thiourea is added to the cooled solution and after the solution has stood in ice for some time with occasional shaking it is noted whether solid kernels of the thiourea are still visible. If not, more thiourea is added. It is important for the quantitative precipitation of the lead that the solution is completely saturated with thiourea and cooled to 0°C. After standing ½–1 hour in ice, the precipitate is filtered through a filter tube with a Jena fritted glass filter and washed with an ice cold 1–2N nitric acid solution which is saturated with thiourea (solid thiourea present at 0°C.). After the washing is finished, the precipitate is strongly sucked, the suction flask replaced with a new one and then the precipitate dissolved in hot water and afterwards washed thoroughly with cold water. The filtrate is now an almost neutral lead nitrate solution which contains thiourea so the lead can immediately be determined as mentioned above.

Precipitation of lead from alloys containing tin and antimony: The alloy is dissolved on the water bath in aqua regia, the solution diluted to 60–100 ml. and 5–8 g. of solid thiourea added to it. On cooling, the lead is precipitated. If it is necessary to add tartaric acid, it is without effect on the lead determination. In the presence of bismuth, the washed precipitate is colored a light yellow which causes noticeable errors. In this case, especially with large amounts of bismuth, it is recommended to dissolve the precipitate in hot water, acidify with nitric acid and reprecipitate the lead with thiourea. The check analysis published by the authors shows excellent agreement.

2. The Determination of Cadmium (46)

The determination is based on the fact that cadmium salts form an insoluble precipitate with thiourea and the so-called "Reinecke salt," $(Cr(NH_3)_2(CNS)_4)NH_4$. A 5% filtered thiourea solution and a filtered "Reinecke salt" solution containing 1% thiourea are used for reagent. The cadmium solution to be tested should not be more than 1N in respect to free mineral acid, and in the presence of large amounts of foreign metals, the acidity should be about 0.1N.

Determination procedure: Sufficient 5% thiourea solution is added to the test solution in the cold so that about a 1% concentration of it is present. To precipitate, the Reinecke salt solution described above is added in excess. When the precipitation is finished, the beaker is placed in ice water and allowed to stand ½–1 hour with occasional shaking. The pale red, finely crystalline precipitate is filtered through a fritted glass filter crucible which was dried at 110°–120°, the beaker and the precipitate washed with ice cold, 1% thiourea solution and then the adhering thiourea removed by washing 3 or 4 times with small portions of ice cold alcohol. After drying at 110–120° the precipitate is weighed.

$F = 0.1247; \log F = 9.09592-10.$

The results obtained by this method are not without errors in the presence of large amounts of other metals. Cadmium can also be determined in the presence of potassium cyanide. This is important in the separation of cadmium from bismuth since according to Strebinger and Ortner (182) bismuth can be determined as BiOI.

2a. Volumetric determination of cadmium (46): The method depends on the fact that the chromium in the precipitate can be oxidized to chromate and titrated by a standard procedure. Two methods can be used to oxidize the chromium.

Oxidation with potassium bromate: The twice precipitated complex is filtered through a fritted glass crucible and washed as usual with the thiourea solution. The crucible is placed in a new suction flask, some solid potassium cyanide (c.p.) added and then washed with hot water which dissolves everything on the filter. 1 ml. of hydrochloric acid, 0.5 ml. of a 1% manganese sulfate solution and sufficient sulfuric acid are added to the solution in a large erlenmeyer flask to bring the acid concentration to about 1N. 2 g. of potassium bromate are added and the solution boiled until no more bromine is evolved. The undissolved manganese dioxide is filtered off, 5 g. of ammonium sulfate added and the solution boiled until it is freed from the excess bromate. Potassium iodide is added to the cooled solution and the iodine titrated with 0.1N thiosulfate.

1 ml. 0.1N thiosulfate = 1.8735 mg. Cd (log F = 0.27266).

Oxidation with sodium peroxide: The cadmium precipitate is transferred to a quantitative filter, washed with 1% thiourea solution, carefully ashed and gently ignited in a nickel crucible until all organic substance is destroyed. The cooled residue is fused with a little sodium peroxide, the crucible placed in a covered beaker and the melt dissolved with a stream of hot water. After the crucible has been removed, the solution is boiled about 15 minutes to destroy the excess peroxide, potassium iodide added, the solution acidified with hydrochloric acid (1:5) and the iodine liberated is titrated with thiosulfate.

III. Pyridine (43)

Aqueous solutions of Cu, Co, Ni, Cd and Zn salts give complex cations with pyridine which form well-defined, insoluble complex salts with thiocyanide ions. These salts correspond to the general formula $(MePy_2)(SCN)_2$.

Mercurous chloride quantitatively forms a white insoluble complex,

$HgCl_2 \cdot Py$ with an excess of pyridine which goes into solution immediately when an alkali cyanide is added, whereby the odor of pyridine arises:

$$HgCl_2Py + 2KCNS = K_2\ (HgCl_2(CNS)_2) + Py.$$

When ammonium thiocyanide and pyridine are added to a lead salt solution in the cold the basic salt, $Pb(OH)SCN$ is quantitatively formed.

These methods attain a certain importance through the fact that mercury can be successfully separated from Cu, Cd, Ni and Fe.

A. INDIVIDUAL DETERMINATIONS

1. Copper (183) (184)

If several drops of pyridine and some ammonium thiocyanide are added to a practically neutral copper solution, then after several shakings, a greenish-yellow precipitate of the composition $(CuPy_2(SCN)_2)$ arises. The precipitate is insoluble in water containing pyridine and ammonium thiocyanide, in 75% alcohol containing pyridine and ammonium thiocyanide and in ether containing pyridine. Short drying at 40–45° does not change the precipitate; likewise drying in vacuum at the usual temperature has no unfavorable effect.

In studying a table of all the metals which react with pyridine and ammonium thiocyanide one sees that this method for the determination of copper is satisfactory only in the presence of mercury, magnesium, the alkaline earths and the alkalies.

Determination procedure: The solution to be tested should be as close to neutral as possible; weakly acid solutions are neutralized with pyridine, strongly acid solutions are evaporated to dryness, taken up with water and pyridine now added to neutralization.

The solution should not contain more than 0.05–0.08 g. of copper; a volume of 75–100 ml. is suitable. Pyridine is added to the solution until it is noticeably azure blue for which 10 drops to 1 ml. of pyridine are generally sufficient. The addition of the pyridine should take place rapidly, since by slow dropping the solution becomes turbid as a result of precipitation of an amine of the copper salt. 0.5 g. of ammonium thiocyanide is added to the blue-colored, clear solution and the solution vigorously stirred. The greenish precipitate formed can be immediately filtered through a porcelain filter crucible. The remainder of the precipitate is then transferred quantitatively with the filtrate into the crucible. Otherwise a wash solution obtained by dissolving 3 g. ammonium thiocyanide and 3 ml. pyridine in 1 l. of distilled water is used.

The precipitate brought quantitatively into the crucible (with the help of a rubber policeman) is now washed 6–8 times with the following solution: 800 ml. of 95% alcohol are mixed with 192 ml. of water and 8 ml. pyridine and 0.5 g. solid ammonium thiocyanide dissolved in this mixture. After the last washing the precipitate is sucked strongly and the last traces of the wash solution removed from the crucible by rinsing 2–3 times with 1–2 ml. portions of absolute alcohol which contains two drops of pyridine per 10 ml. of solution. Finally the precipitate is washed thoroughly with ether which contains two drops pyridine per 20 ml. The precipitate is sucked strongly, the crucible placed in a vacuum desiccator over P_2O_5 and after ten minutes in the evacuated desiccator, the precipitate can be weighed.

$F = 0.18817$; $\log F = 9.27455-10$.

If one prefers, the precipitate may be freed from the last traces of wash solution by drying (at most 20 min.) in a drying oven at 40–45°. After the removal from the oven, the crucible must be cooled 10–15 minutes in a desiccator over P_2O_5.

According to the check analyses announced, the method gives faultless results.

The method (183) was also worked out as a micro method whose basis is the extraction of the complex salt formed with chloroform. By evaporation of chloroform in the vacuum desiccator over P_2O_5 one obtains the formula pure compound. Since the determination requires a special apparatus and the method is of hardly any importance for microanalysis, this short general view should suffice.

According to A. Tettamanzi (185) the reaction can be carried out as a rapid method only by volumetric determination of the excess thiocyanide ion: A 15% aqueous pyridine solution, and then from a burette a determined volume of 0.1N potassium thiocyanide solution is added to the neutral or weakly acid copper solution in a 250 ml. measuring flask. The precipitate is allowed to stand for one half hour, the solution diluted to the mark, filtered through a dry filter and 200 ml. of the filtrate titrated with 0.1N silver nitrate after acidifying with nitric acid and adding ferric ammonium sulfate solution.

1 ml. 0.1N KCNS..........3.1785 mg. Cu.

The excess of potassium thiocyanide solution should be about one-fifth to one-fourth of the required amount.

2. Cadmium (43) (186)

By adding ammonium cyanide and pyridine to cadmium salts in the cold, a white, finely-crystalline precipitate, $(CdPy_4)(SCN)_2$, is formed.

This compound loses (at ordinary temperature, slowly, at 40–45°, in about one hour) two molecules of pyridine and changes into the very stable dipyridine-cadmium-thiocyanide appearing as long, gleaming, colorless needles of the formula $(CdPy_2)(SCN)_2$. This same salt is obtained by precipitating a cadmium salt solution containing alkali thiocyanide with pyridine in the hot.

The complex salt is insoluble in water containing pyridine and alkali thiocyanide, in 25% alcohol containing pyridine and alkali thiocyanide and in the ether containing pyridine.

Determination procedure: 0.5–1 g. of solid ammonium thiocyanide is added in the cold to the neutral cadmium solution whose volume should be about 50–100 ml. and the solution heated to boiling. The cadmium is now precipitated from the hot solution with 1 ml. of pyridine stirring well several times and the solution allowed to cool. The precipitate gradually comes out in beautiful long prisms. After complete cooling it is filtered through a filter crucible and the precipitate quantitatively transferred into the crucible by means of the following wash solution: 5 ml. pyridine + 3 g. ammonium thiocyanide diluted to a liter. Then it is washed with 25% alcohol containing pyridine and ammonium thiocyanide, (25 ml. 95% alcohol plus 73 ml. H_2O plus 2 ml. Py plus 0.1 g. NH_4CNS), once or twice with 1 ml. portions of absolute alcohol containing pyridine (1 ml. Py per 10 ml. alcohol) and finally 5–6 times with ether containing pyridine (2 drops pyridine per 15 ml. ether). The precipitate is dried about ten minutes in a vacuum desiccator and weighed.

$F = 0.2907; \log F = 9.46345-10.$

Ammonia salts, in general, do not disturb the determination. However the precipitate is somewhat soluble in ammonium chloride and rather soluble in ammonium acetate. In concentrated solutions the precipitate comes out immediately on the addition of pyridine. However it is contaminated with tetra pyridine-cadmium-thiocyanide. Under these conditions, the solution is diluted with water, boiled until the precipitate has almost completely dissolved and allowed to cool.

According to R. Ripan (187), the cadmium can also be determined volumetrically by this method. The cadmium is precipitated with a measured excess of 0.1N ammonium thiocyanide solution, the precipitate filtered off and the excess of ammonium thiocyanide back titrated with 0.1N silver nitrate solution.

The determination of copper and cadmium in this way is significant because it can be carried through easily in an hour. Therefore, it possesses a certain importance as a rapid method.

3. Lead (188)

The determination depends on the insolubility of the basic lead thiocyanide in 95% alcohol, in ether and in water containing pyridine and alkali thiocyanide. In the presence of ammonium salts the salt is slowly changed and gradually goes into solution.

Determination procedure: A solution of 2 g. of ammonium thiocyanide and 1 ml. of pyridine in several milliliters of water is added to the lead solution (not more than 50 ml. volume) and the solution stirred several times. The amount announced is sufficient for the precipitation of up to about 0.3 g. Pb. For larger amounts of lead, correspondingly more precipitant is used (about 3 g. NH_4CNS and 1.5 ml. Py). By pouring this mixture into the lead solution, a white milky precipitate is formed at once which is immediately filtered through a filter crucible after stirring 4–5 times without waiting for settling and coagulation. The remaining precipitate is transferred with water containing pyridine and ammonium thiocyanide (4 g. NH_4CNS + 2 ml. Py in 200 ml. water) into the crucible, the precipitate washed three or four times with 95% alcohol and after this 4–5 times with ether. The precipitate is sucked as dry as possible and dried for 5–6 minutes in the vacuum desiccator at room temperature. Drying for 5–10 minutes at 40° has no effect but in this case the sample must be allowed to cool fifteen minutes in the desiccator before weighing.

F = 0.7340; log F = 9.86570–10.

The determination can be carried through in about 20 minutes.

4. Nickel (183) (43) (189)

Nickel forms a sky blue complex compound with pyridine and ammonium thiocyanide which has the formula of a tetrapyridine-nickel-thiocyanide, $(NiPy_4)(SCN)_2$. The compound is insoluble in alcohol containing pyridine and ammonium thiocyanide and in ether containing pyridine.

Determination procedure: 0.5 g. ammonium thiocyanide is added to the nickel solution (100 ml. volume) for each 0.1 g. Ni present, the solution heated to boiling and precipitated with 1 ml. of pyridine for each 0.1 g. Ni. The flame is immediately removed and the solution stirred until the precipitate comes down in gleaming sky blue prisms. The precipitate comes down either immediately or after several minutes, depending upon the nickel concentration.

After complete cooling of the solution (the precipitate is somewhat soluble in the hot) it is filtered through a filter crucible, the rest of the precipitate transferred to the crucible with the filtrate or with water containing pyridine and ammonium thiocyanide (4 g. NH_4CNS + 6 ml. Py per 1000 ml. of water) and then washed four or five times with the following wash solution: 370 ml. 95% alcohol + 615 ml. water + 15 ml. pyridine + 1 g. NH_4CNS. The precipitate is strongly sucked and the walls of the crucible washed quickly (on account of the slight solubility of the precipitate) with two 1 ml. portions of alcohol containing pyridine (0.5 ml. pyridine per 10 ml.). Finally the precipitate is washed 5–6 times with ether containing pyridine (2 drops of pyridine per 20 ml. ether), again sucking strongly and then weighed after drying in the desiccator at room temperature. The results are very good.

$F = 0.1195$; $\log F = 9.07737-10$.

4a. Volumetric determination of nickel (43): The method is based on the precipitation of nickel as $(NiPy_4)(SCN)_2$ with a measured excess of ammonium thiocyanide solution which is back titrated after the precipitation. From the amount of thiocyanide used, the nickel can be calculated since 2 CNS' corresponds to 1 Ni.

Spacu and Ripan (43) have developed two practical titration procedures.

(a) The sample in a 100–150 ml. beaker is dissolved in 25–30 ml. of water and 8–10 drops of pyridine added. A measured excess of 0.1N ammonium thiocyanide solution is allowed to flow into the beaker and the solution heated almost to boiling with constant stirring. After complete cooling the supernatant liquid is filtered off and the precipitate washed several times by decantation using a total of 100–150 ml. of 5% aqueous pyridine. Filtrate and wash water are placed in an erlenmeyer flask, acidified with dilute nitric acid and an excess of 0.1N silver nitrate added. The excess silver can now be titrated with ammonium thiocyanide (using ferric ammonium sulfate as indicator). By a simple calculation the excess thiocyanide and also the amount of nickel present can be determined.

1 ml. 0.1N NH_4CNS solution..... ....2.934 mg. Ni.

(b) The weighed sample is transferred to a 100 ml. measuring flask, dissolved in 50–60 ml. of water and the nickel precipitated as in (a). After this the contents of the flask are diluted to about 75 ml., the flask placed on a cold water bath and slowly heated to boiling. During the heating the flask is shaken from time to time. After cooling, the flask is filled to the mark, mixed thoroughly and the solution filtered through a dry filter into a dry flask. An aliquot portion is removed from the filtrate with a pipette and then titrated as in (a).

5. *Cobalt (190)*

Cobalt salts to which alkali thiocyanide and afterwards pyridine are added in excess form a peach-bloom colored precipitate of the composition $(CoPy_4)(SCN)_2$ which is somewhat soluble in water. In ethyl alcohol and ether it is rather soluble but only traces are dissolved in amyl alcohol. In methanol and chloroform the precipitate is easily soluble. It is completely insoluble in alcohol containing alkali thiocyanide and pyridine, in ether containing pyridine, and only traces are dissolved in absolute alcohol containing pyridine.

Determination procedure: 0.5 g. ammonium thiocyanide for each 0.1 g. cobalt is added to the cobalt solution whose volume should be about 75–80 ml. (excess is not harmful), the solution heated to boiling and 1 ml. of pyridine added. In the presence of very much cobalt, 1 g. ammonium thiocyanide in excess and a total of 2–3 ml. of pyridine are added to the solution. After the reagents have been added, the flame is immediately removed. (During the pouring in of the pyridine one stirs several times in order to avoid evaporation losses of the pyridine.) The still clear solution is allowed to cool, whereby the complex salt slowly precipitates in peach-bloom colored, gleaming prisms. If the precipitate shows a blue color on the walls of the beaker (a compound poor in pyridine), then it is washed into the beaker with water, whereby the blue color immediately disappears. The precipitation of the complex is accomplished by stirring several minutes; in the presence of considerable cobalt, the precipitate comes down immediately on the addition of pyridine. However, it is of fine crystals.

After cooling, the solution can be immediately filtered through a porcelain filter crucible. The precipitate remaining in the beaker is transferred to the crucible with the filtrate, or if this is needed for further determination, with a wash solution which contains 7 ml. of pyridine and 5 g. ammonium thiocyanide per liter. The precipitate is now washed in the crucible 5–6 times with the following wash solution: 130 ml. 95% alcohol + 855 ml. water + 15 ml. pyridine + 1 g. NH_4CNS. The precipitate is sucked strongly and washed once or twice with absolute alcohol (which contains 2 ml. pyridine per 25 ml.). The alcohol is distributed over the whole crucible and precipitated as well as possible with a small glass rod in order to remove the remaining water. Finally the precipitate is washed 8–10 times with ether which contains four drops pyridine per 30 ml. The precipitate is again sucked strongly, the outside wall of the crucible washed with ether, the crucible placed into a vacuum desiccator, then evacuated and dried 3–10 minutes—according to the amount of the precipitate.

F = 0.12002; log F = 9.07925–10.

Filtration and washing of the precipitate does not take up more than 5–10 minutes, the drying in the vacuum is finished even with large amounts of precipitate in ten minutes. The results are very satisfactory.

If very large amounts of ammonium salts are present then the precipitate is somewhat soluble. Very strongly acid solutions are first evaporated to dryness and then dissolved in water for use. Pyridine is added in the cold to weakly acid solutions until the appearance of a precipitate, the solution heated until the precipitate is just dissolved, then 1 ml. more pyridine added and the flame immediately removed.

In spite of the exactness and rapidity, one will scarcely ever use this method since nickel, zinc, etc. interfere.

6. Zinc (43)

By adding alkali thiocyanide and a little pyridine to neutral zinc salt solutions a crystalline white precipitate of the composition, $ZnPy_2(SCN)_2$, is obtained on shaking. The sensitivity of the reaction is rather great—0.05 mg. Zn can be detected in 100 ml. water. With this small concentration it is absolutely necessary that the thiocyanide be added before pyridine since $Zn(SCN)_2$ will be formed first which then reacts with the pyridine under the formation of an amine. Besides this, it is best to avoid an excess of pyridine in which the precipitate is rather easily soluble.

Determination procedure: An excess of solid ammonium thiocyanide (0.25 g. NH_4CNS for 0.1 g. Zn) is added to the aqueous neutral zinc salt solution whose volume should be at most 35 ml. for 0.1 g. Zn and now pyridine is added in very slight excess (for 0.1 g. Zn about 6–7 drops of pyridine). The solution is vigorously stirred, allowed to stand 15 minutes and then filtered through a quantitative filter. The precipitate is washed with cold water which contains 0.3 g. NH_4CNS, 0.2 g. $(NH_4)_2SO_4$ and six drops of pyridine in 100 ml. Since the amine cannot be weighed, but must be ignited to the oxide, the washing can be omitted when, for example, only ammonium salts are present besides the zinc.

The check analyses announced by Spacu (43) show good agreement with values found electrolytically. It is, however, questionable whether the method can give correct values in the investigation of solutions of unknown zinc content.

B. SEPARATIONS

The ability of mercurous salts to form soluble complex salts with alkaline thiocyanide which are not changed by pyridine may be used for separating mercury from the metals which form insoluble amines with alkaline thiocyanide and pyridine.

1. Separation of Cadmium from Mercury

Separation procedure (191): Ammonium thiocyanide is added in excess to the neutral solution of both salts, the solution warmed gently and dilute pyridine (1:3) added to it. After the cooling the precipitate is allowed to stand at least one hour in the cold and then decanted through a filter wet with water containing pyridine and ammonium thiocyanide. (The wetting of the filter with this wash solution is necessary because otherwise the precipitate is not quantitatively held by the filter.) The precipitate is now transferred on to the filter with the wash solution and washed well. Since the $CdPy_2(SCN)_2$ always retains small amounts of mercury salts, the precipitate is dissolved in the least possible hydrochloric acid (1:10), the solution neutralized with ammonia until the odor of pyridine is just apparent, ammonium thiocyanide added (whereby the cadmium as a rule again precipitates) and the precipitation completed with pyridine. After allowing the precipitates to settle, it is decanted and filtered as announced above.

From the combined filtrates the mercury can be determined by passing in H_2S in the usual way.

The cadmium is determined simplest as the sulphate by dissolving the precipitate on the filter with dilute nitric acid evaporating the solution in a weighed quartz crucible and destroying the organic substance by gentle heating. Dilute sulfuric acid is added to the residue and then the excess sulfuric acid removed by evaporation on an air bath.

2. Separation of Iron from Mercury (192)

Basis of the method: Mercury forms a white complex salt with pyridine that dissolves in alkali thiocyanide. Ferric salt solutions are quantitatively precipitated by pyridine as ferric hydroxide in the presence of alkali thiocyanide.

$$Fe(SCN)_3 + 3C_5H_5N + 3H_2O = Fe(OH)_3 + 3C_5H_5N \cdot SCNH$$

Separation procedure: About 1 g. ammonium thiocyanide is added (for 0.3 g. of metal) to the solution of both metals made up to a volume of 100 to 150 ml. and then pyridine added dropwise to the solution until the red color changes into yellow brown. Then three more drops of pyridine are added, the solution heated almost to boiling and after settling the precipitate is filtered and washed with hot water. The iron is then determined as Fe_2O_3.

The mercury is precipitated out of the filtrate as the sulfide by passing in H_2S.

The results are satisfactory.

If a nitric acid solution is present, then the nitric acid is removed by evaporation (with the addition of potassium chloride) and the residue dissolved in water.

3. Separation of Copper from Mercury (193)

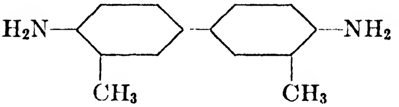
The solution of both metal salts whose volume should be about 150 ml. is heated to boiling and pyridine added in excess so that the solution is colored distinctly dark blue. By addition of solid ammonium thiocyanide in excess (about 8–10 times the weight of the original sample) and by vigorous stirring, the copper precipitates quantitatively as a green, flocculent precipitate while the mercury remains in solution as a complex thiocyanide. After cooling for about 1 hour, the precipitate is filtered out on a filter, washed well with cold water which contains 5 g. ammonium thiocyanide and 5 ml. pyridine per liter, then dried in a weighed porcelain crucible and carefully ignited to CuO. (Concerning the ignition of copper compounds containing sulfur to copper oxide, compare with the discussion on page 19). Spacu (192) announces, that the heating of the CuS must be done with care, "so that a partial fusion could not occur and prevent complete transformation into the oxide."

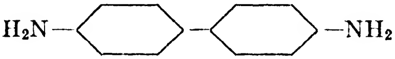
In the filtrate the mercury can, after acidification with hydrochloric acid, be precipitated and determined as the sulfide.

The values obtained by this method compare excellently with the check analyses announced by Spacu. It appears, however, that the change of copper precipitate into oxide possesses certain difficulties. According to the announcement of Springer (29), one has to expect that the copper oxide obtained for weighing is contaminated by sulfate.

4. Separation of Iron from Copper and Nickel (194)

After oxidizing the iron, pyridine is added in excess to the solution which contains iron and nickel. The precipitated iron oxyhydrate is filtered off and the nickel precipitated from the filtrate with more pyridine and some potassium thiocyanide, washed with alcohol and ether and weighed (see page 160). To separate iron from copper, pyridine is added dropwise to the solution until no more iron precipitates and the supernatant liquid is blue. The iron precipitate is filtered off and the copper determined in the filtrate as $(CuPy_2)(CNS)_2$ by adding more pyridine and some potassium cyanide (see page 157).

IV. Tolidine  and Benzidine



If several drops of an alkali thiocyanide solution and then at most two drops of a freshly prepared 2% alcoholic solution of tolidine are added to a very dilute solution of any copper salt, then on shaking, a blue, flocculent precipitate immediately arises which is very characteristic. The color of the precipitate is similar to that of prussian blue.

The salt which has the formula, $(CuTldn)(SCN)_2$,* is insoluble in water but easily soluble in alcohol. Therefore, a greater amount than two drops of the 2% reagent solution for reaction must be avoided since otherwise no precipitate arises, but only a solution of dark blue color.

The reaction is very sensitive. It allows, in absence of Fe^{+++} ions, the detection of copper in a dilution of 1:500,000. Thus 0.2 mg. of copper in 10 ml. water can be detected immediately by the appearance of a flocculent blue precipitate.

The reaction is, however, of no value as a gravimetric method since the solubility of the salt in aqueous alcohol is too great. In the most favorable cases, the values are 0.06–0.3% too low.

If benzidine is used instead of tolidine then an analogous reaction takes place. The $(CuBzdn)(SCN)_2$† arising is practically insoluble in aqueous alcohol. However, the amine is never precipitated as the formula pure compound, but is always contaminated by small amounts of ammonium thiocyanide and benzidine. For this reason the precipitate must be ignited to CuO whereby the advantage of a more favorable conversion factor is lost. However, since the amine precipitates so well perhaps the method could be used as a "semimicro" determination, especially since from the check analysis of the authors, (38) one might conclude that the CuO finally obtained is apparently almost free of sulfates. It can naturally not be decided whether these very well agreeing values did not result from a compensation of errors.

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* Tldn = Tolidine.

† Bzdn = Benzidine.

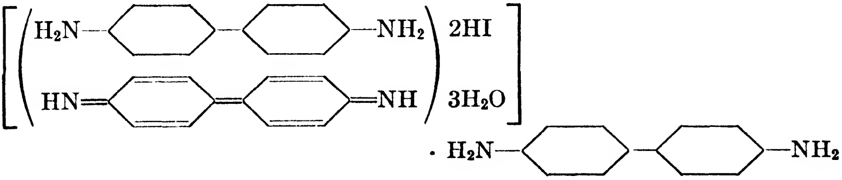
The following **procedure** has been found practical for the precipitation of the copper as $(CuBzdn)(SCN)_2$.

40–50 ml. of a 1% ammonium thiocyanide solution and 10–20 ml. of a 2% alcoholic benzidine solution are added in the cold with stirring to the aqueous solution of the copper salts in 50–70 ml. of water (at most 0.01 g. Cu). (The benzidine should be present in only a slight excess. However, a 4–5 fold excess of ammonium thiocyanide solution does not impair the determination.) After addition of the benzidine solution, a voluminous precipitate having a dark blue color is formed immediately. One can then filter right away through a black ribbon filter and wash with water. If only ammonium salts are present, the washing may be omitted since all ammonium salts will surely be evaporated (or decomposed) during the following transformation of the precipitate into CuO.

The precipitate can either be ignited in a porcelain crucible when still wet or first be dried with the filter in the desiccator and then be ignited.

The micro determination is carried out by Spacu and Macarovici (44) in an exactly analogous manner. Since the method is of hardly any significance as micro-method, a detailed description is not given.

In this connection the following should be mentioned: Spacu (44) announces also that $(CuBzdn)I_2$ is well suited for the qualitative detection of copper. A check made by A. Tettamanzi (195) showed that when copper is precipitated by benzidine and potassium iodide, the blue precipitate does not correspond to the composition $(CuBzdn)I_2$. Rather it is found that the (copper free) precipitate is an oxidation product of benzidine whose structure corresponds nearly to the product formed by the reaction of chlorine on benzidine. According to Schlenk (196), chlorine and benzidine react with the formation of a meriquinoid compound which possesses the following structure:



As is well known, copper salts and potassium iodide form elementary iodine according to the equation:

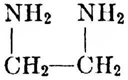
$$CuSO_4 + 2KI = K_2SO_4 + CuI + I$$

which acts upon benzidine in the described way. This conception was proven through the fact that benzidine and iodine (or bromine) in the absence of copper salts form a similar dark blue precipitate.

Consequently copper has been detected by an "induced" reaction. G. Spacu and C. G. Macarovici (197) have studied the objection of A. Tettamanzi (191) and point out that a blue precipitate is obtained in the presence of copper ions even in a dilution of 1:2,000,000 while benzidine and iodine form a blue color only in concentrations of 1:100,000 which immediately disappears. This phenomena is offered by the authors (193) as proof of the formation of the complex amine, Cu-Bzdn-I_2, in the presence of copper ions. If the reaction is done with SCN′, SeCN′, Br′, Cl′, F′, CNO′ or CN′ in place of I′, then it can be established that the sensitivity decreases from iodine to chlorine.

For analytical purposes it was shown that the copper ion is completely precipitated.

V. Ethylenediamine



$$\begin{array}{cc} NH_2 & NH_2 \\ | & | \\ CH_2 - & CH_2 \end{array}$$

(40)

As is commonly known, ethylenediamine forms a complex cation with copper. With the complex anions, $(HgI_4)''$ and $(CdI_4)''$, these cations form insoluble complex salts which are suited for the determination of mercury, cadmium and copper as well as for the separation of copper from mercury. Since the precipitates are insoluble in 95% alcohol and in ether, the drying time can be essentially shortened by washing the precipitate with alcohol and ether; thus the determinations may be considered rapid methods. A solution of $(Cuen_2)(NO_3)_2$* which is prepared in the following manner is used as reagent.

An aqueous solution consisting of one part of copper nitrate and two parts of ethylenediamine is heated on the water bath until a crust has formed on the surface of the violet-blue liquid. After cooling, the precipitated crystals are filtered out under suction and washed several times with alcohol and ether. The crystals correspond to the composition $(Cuen_2)(NO_3)_2 \cdot 2H_2O$. According to the experiments made by Spacu (40) it is absolutely essential to use nitrate as reagent. The preparation of the crystalline salts may also be omitted since an excess of copper in the reagent solution does not do any harm. Hence in order to prepare the reagent solution, copper sulfate solution should be added to an aqueous solution of ethylenediamine until the dark blue violet color characteristic for the complex $(Cuen_2)$ arises.

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* en = ethylenediamine, $NH_2—CH_2—CH_2—NH_2$.

1. Determination of Mercury (40)

This determination is based upon the precipitation of the mercury as an insoluble complex salt, $(HgI_4)(Cuen_2)$. The reactions occurring during this precipitation are summarized by the following sets of equations:

$$HgCl_2 + 4KI \rightarrow K_2(HgI_4) + 2KCl$$

$$K_2(HgI_4) + (Cuen_2)(NO_3)_2 = (Cuen_2)(HgI_4) + 2KNO_3$$

A large excess of potassium iodide must be used to buffer completely the dissociation of the anion,

$$(HgI_4)'' \rightleftarrows 2I' + 2HgI$$

otherwise the complex amine which was first prepared by Spacu (198) $(HgCl_4)(Cuen_2)$ or $(HgCl_3)_2(Cuen_2)$ could be formed.

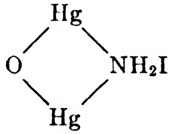
Determination procedure: Potassium cyanide is added to the neutral or weakly ammoniacal mercury solution whose volume may be any amount between 80 and 500 ml., the solution heated nearly to boiling and the mercury precipitated with a boiling, concentrated solution of $Cuen_2(NO_3)_2$ in water. While cooling beautiful, large, plate-like crystals of a blue violet color slowly separate from the solution. After complete cooling the solution is filtered through a porcelain filter crucible and the precipitate quantitatively transferred into the crucible with the following wash solution: 1 g. of KI + 1 g. $(Cuen_2)(NO_3)_2 2H_2O$ in a liter of distilled water. The precipitate is washed in the crucible three to four times with this wash solution, then washed 3-4 times with 2 ml. portions of 95% alcohol to remove droplets of the liquid adhering to the crucible wall, and finally 2 4 times with 2 ml. portions of ether. After sucking dry, the precipitate can then be weighed after 5-10 minutes of drying in the vacuum desiccator. $F = 0.2249$; $\log F = 9.35199-10$.

The precipitate is unchanged in both air and vacuum and precipitates formula pure even in the presence of ammonium salts. Consequently the method may also be used advantageously for the determination of mercury out of solutions of mercury in aqua regia, as they are usually obtained in the course of a mineral analysis.

Ammonia is added in the presence of an indicator to the solution containing mercury (the volume should be 100–200 ml. for 0.3 g. Hg.) until the solution has become weakly alkaline. (A small excess of ammonia does not impair the results of the determination!) To the solution thus prepared a large excess (about 2%) of potassium iodide is added, the solution is then heated to boiling and precipitated with the reagent in the described manner. After completion of the precipitation, the solution is diluted with distilled water until the volume is increased by about $\frac{1}{4}$, allowed to cool and the above procedure followed exactly.

M. Straumanis and A. Cirulis (199) report favorable results using a procedure slightly different from that announced by Spacu.

This method appears to be of special importance because, as compared with Volhard's method, it may be carried through in a far shorter time. Theoretically it is interesting to note that also in ammoniacal solution the complex salt precipitates formula pure. Therefore the formation of the $(HgI_4)(Cuen_2)$ is preferred to the formation of



2. Determination of Copper

The method may, of course, also be used for the determination of copper. After neutralizing with ammonium hydroxide, ethelyenediamine is added to the copper solution until the well known color of the complex arises (p. 168). The solution is heated to boiling and then a solution of potassium iodomercurate, $K_2(HgI_4)$, added in excess. The further treatment of the precipitate takes place exactly according to the procedure given for the determination of mercury. As wash solution about a 1% solution of $K_2(HgI_4)$ is used; at the end, the precipitate is freed from the adhering wash solution by the use of alcohol and ether and finally weighed after short drying in the vacuum desiccator.

$F = 0.07126$; $\log F = 8.85289-10$.

3. Determination of Cadmium (200)

Analogous to mercury, cadmium forms a complex salt completely insoluble in water which contains about 1% KI and 0.3 to 0.5% of $Cuen_2$. Since the salt is also insoluble in alcohol and ether, the determination can be carried through in a very short time. Contrary to the determination of mercury, ammonium salts are disturbing here as they prevent the quantitative precipitation. The precipitate is also slightly soluble in strongly ammoniacal or ethylenediamine solutions.

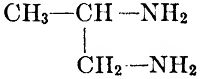
Determination procedure: An excess of potassium iodide is added to the cadmium salt solution whose volume should be about 100 to 300 ml. The solution is heated to boiling and precipitated with a concentrated solution of $(Cuen_2)(NO_3)_2$ in water. During cooling the precipitate separates in beautiful large crystals which are filtered out through a porcelain filter crucible after cooling is complete. The precipitate, which is brought into the crucible with a wash solution containing 1 g. KI and 0.3 g. $(Cuen_2)(NO_3)_2 \cdot 2H_2O$ in 100 ml. water, is washed several times with the same wash water. Then it is washed 4–6 times with 2 ml. portions of ether. After 5–10 minutes of drying in the vacuum desiccator the precipitate can be weighed.

$F = 0.1396$; $\log F = 9.14470 - 10$.

The method also allows the **determination of copper in the presence of mercury.** For this purpose ammonium hydroxide is added to the acid solution of both metals until the solution is almost neutral and then it is made alkaline with ethylenediamine. The solution is now heated to boiling, KI and $(Cuen_2)(NO_3)_2 \cdot 2H_2O$ added in excess, the solution allowed to cool and exactly the same procedure as announced for mercury followed.

In another part of the test solution the copper is precipitated according to the procedure described on page 170.

VI. Propylenediamine (41) (42)

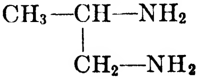


$$\begin{array}{l} CH_3—CH—NH_2 \\ \qquad\;\; | \\ \qquad CH_2—NH_2 \end{array}$$

Just like ethylenediamine, propylenediamine forms a complex cation with copper which forms analogous complex salts with the complex anions, (HgI_4) or (AgI_2), that are very well suited for the determination of smaller amounts because of their insolubility and of their favorable conversion factor.

Preparation of the reagent: The $(Cupn_2)SO_4$* is extremely soluble in water, so that it has not yet been isolated in the solid state. Therefore, immediately before use, an aqueous solution of copper sulfate is mixed with propylenediamine in the ratio:

1 mol $CuSO_4 \cdot 5H_2O$: 2 mols



$$\begin{array}{l} CH_3—CH—NH_2 \\ \qquad\;\; | \\ \qquad CH_2—NH_2 \end{array}$$

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* pn = propylenediamine.

1. Determination of Mercury (41)

Potassium iodide in excess is added to the neutral or weakly ammoniacal mercury salt solution whose volume should be between 100–250 ml., the solution heated to boiling and then a boiling concentrated solution of $(Cupn_2)SO_4$ added to it. The solution is cooled by placing the beaker in cold water whereby beautiful, large, tubular crystals of a dark violet color precipitate. After cooling is complete the solution is filtered through a porcelain filter crucible and the precipitate transferred to the crucible by means of a wash solution which contains 1 g. of potassium iodide and 1 g. $(Cupn_2)SO_4$ per liter. The crucible walls are washed 3–6 times with 2 ml. portions of 96% alcohol and then 2–4 times with 2 ml. of ether. After drying about 10 minutes in the vacuum desiccator, the precipitate can be weighed.

F = 0.2181; log F = 9.33854–10.

2. Determination of Silver (42)

An excess of potassium iodide is added to the neutral or weakly ammoniacal silver nitrate solution until the silver iodide is completely in solution. (A large volume of silver nitrate solution is to be avoided since then a disproportionately large amount of potassium iodide must be added to dissolve the silver iodide.) A freshly prepared, concentrated, hot reagent solution is added to the boiling hot silver solution and the solution allowed to cool. The pale violet crystals of the silver compound begin to precipitate from the warm solution. The precipitate is filtered through a porcelain filter crucible, washed with water containing 1% KI and 0.5% $(Cupn_2)SO_4$ and then with alcohol and ether. After 10 minutes drying in the vacuum desiccator, the precipitate is weighed. F = 0.2307; log F = 9.36310–10.

Weakly acid silver solutions can be neutralized with ammonia, strongly acid solutions must be evaporated on the water bath to dryness, the residue dissolved in water and completely neutralized with ammonia. The solution should not contain large amounts of ammonium salts since then the silver salt is somewhat soluble. For the same reason, a large excess of reagent solution is to be avoided.

The high sensitivity, 1:200,000, and the favorable conversion factor make the above procedure applicable to **micro analytical** practice. The precipitate is filtered through a micro filter crucible according to König (201). The analyses published by the authors for the micro application check to about 0.4γ.

Also according to this method, mercury can be determined in the presence of copper without difficulty. The procedure is very similar to that described for ethylenediamine on page 171.

Finally, the possibility of **determining bismuth** is pointed out (202). The method depends on the precipitation of bismuth as a complex salt of the following formula:

$$(BiI_4)\ (Coen_2(SCN)_2)\ \text{or}\ (BiI_4)_2(Coen_3)I.$$

D. METAL ADSORPTION COMPOUNDS AS PRECIPITANTS

A. R. Powell and W. R. Schoeller (48) first made use of the fact that **tannin** formed insoluble adsorption compounds with certain metal hydroxide salts to separate tantalum from niobium. They found that the complex tantalum oxalic acid could be hydrolyzed in boiling, weakly acid solution with tannin, but a tannin adsorption compound is formed which quantitatively removes the tantalum as a sulfur yellow precipitate. Niobium oxalic acid is precipitated in a similar way only a higher tannin concentration and a lower hydrogen ion concentration is necessary; a bright red niobium adsorption complex is formed. However, the precipitation of the niobium complex is reversible; by adding oxalic acid to the boiling solution, the tannin-niobium complex goes into solution probably forming the complex $Nb_2O_5 \cdot 3(NH_4)_2O \cdot 6C_2O_3 \cdot 3H_2O$ (203).

If a solution containing both metals in the form of the oxalate complexes is heated with tannin to boiling, the tantalum-tannin complex precipitates quantitatively. However, the precipitate practically always contains niobium which is apparent from the color of the precipitate. Small amounts of niobium change the color of the tantalum complex from yellow to orange. The amount of niobium coprecipitated depends on the concentration of the tantalum and of the niobium and on the pH of the solution. The pH concentration necessary for complete precipitation of the tantalum complex is not low enough to keep the niobium complex completely in solution. Thus, only with low niobium concentration is it possible to obtain the tantalum free from niobium by one precipitation. Also the adsorption of niobium by the precipitate is a further source of error.

To avoid these errors, it is necessary to precipitate the tantalum complex fractionally.

Also, the different effect of beryllium ions on ammonium acetate-tannin should be mentioned here. On boiling weakly acid or neutral beryllium **sulfate** solutions with ammonium acetate-tannin solution, the solution remains completely clear; the solution, as already mentioned, probably contains the beryllium in the form of a complex salt. If the same experiment is done with a beryllium **chloride** or **nitrate** solution, then a small amount of a practically insoluble compound is precipitated. With very concentrated beryllium **chloride** solutions, an insoluble precipitate immediately comes down in the cold on the addition of the ammonium acetate-tannin solution* (204).

In completely neutral solutions, beryllium salts are precipitated by tannin as an insoluble adsorption compound which is suitable for precipitating beryllium in the presence of alkalies.

1. Separation of Aluminum from Beryllium

Basis of the method: A 3% solution of tannin in a cold saturated ammonium acetate solution precipitates only aluminum as an insoluble adsorption compound while the beryllium, so long as it is the sulfate form, remains in solution.

Preparation of the reagent: 3 g. of purest tannin (a purity test is absolutely necessary!) is dissolved in 100 ml. of a cold saturated solution of ammonium acetate in water. Since this solution does not keep very long, it is best to prepare it shortly before use. The solution should be, at the worst, slightly yellowish and completely clear; brownish solutions are discarded.

Purity of the tannin: Inorganic contaminants (principally zinc) must be determined and also sugar and dextrin must be tested for.†

1. Inorganic contaminations: 4 g. of tannin are placed in a suitable crucible (a quartz crucible or dish is best) and ignited. The residue should not be more than 5 mg. The residue is dissolved in 2 ml. of acetic acid, the solution diluted with 8 ml. of water, filtered through a quantitative filter and hydrogen sulfide water added to the clear filtrate. At most, a slight opalescence should arise.

2. Test for sugar, dextrin: If 10 ml. of an aqueous tannin solution

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* Also the analogous reaction of zirconium salts with oxalic acid should be mentioned here. As is well known, zirconium oxychloride solutions are precipitated by oxalic acid, while in zirconium sulfate solutions or in zirconium oxychloride solutions which contain sodium sulfate the precipitation does not take place. R. Ruer (*Z. anorg. allgem. Chem.*, **42**, 87 (1913)) has explained this anomalous behavior by the fact that in sulfate solutions a complex ion $ZrO(SO_4)''_2$ is present which no longer shows all of the typical zirconium reactions.

† Compare E. Merck: Testing Chemical Reagents for Purity.

(1:5) is mixed with 10 ml. of alcohol (about 85% by weight), then this mixture must remain clear an hour; after the further addition of 5 ml. of ether, no turbidity should appear.

3. **Determination of the water content:** When the tannin is dried to constant weight at 100°, not more than a 12% loss in weight is permissible.

4. **The determination of the actual tannin content** is carried out according to Loewenthal v. Schröder (Lunge-Berl, Chemisch-technische Untersuchungsmethoden, 7th edition, Vol. IV, p. 402).

Separation procedure: The weakly sulfuric acid solution of the sulfate is diluted to about 500 ml. with hot water for 0.1 g. Al_2O_3; if more than 0.1 g. Al_2O_3 is present, the solution is diluted to a 600–800 ml. volume. The reagent solution warmed to about 80° is added to the dilute solution all at once and the solution stirred, whereby the aluminum compound immediately precipitates. The solution is boiled 2 minutes, then the flame is removed and the precipitate allowed to settle in the cold. Then several drops more of precipitant are added to make sure the precipitation is complete.

The further treatment of the precipitate depends on the amount of aluminum present.

a. When not more than 0.06 g. Al_2O_3 is present, the precipitate is filtered through a black band filter, washed with warm 5% ammonium acetate solution, the filter and the precipitate dried in the oven and then ignited in a platinum crucible to Al_2O_3. By fuming the residue 2 or 3 times with several drops of nitric acid, a pure white aluminum oxide is formed.

b. If more than 0.06 g. Al_2O_3 is present, the precipitate is filtered through a dense fritted glass crucible, washed with ammonium acetate solution and then dissolved off the crucible with nitric acid (1:3). In order to completely oxidize the tannin, several drops of fuming nitric acid are added whereby the solution finally becomes completely colorless. After dilution the aluminum is precipitated with ammonia, filtered and the hydroxide is ignited to the oxide. If the oxide should not be pure white, it is smoked several times with nitric acid and again ignited. The oxyquinoline method of Berg also works very well in this case.

Beryllium is determined in the filtrate according to one of the usual methods.

It often happens that the solution containing the aluminum and beryllium is colored yellowish by the addition of ammonia though the organic substances have been oxidized. This is due to the formation of small amounts of nitro products and has no effect on the determination.

The results are very satisfactory.

2. Separation of Beryllium from Iron

To the solution of both metal salts whose volume should be about 500 ml., an excess of ammonium acetate (40–50 g.) (50, p. 678) and 20–25 g. of ammonium nitrate are added. The solution is then acidified by adding 1.5 ml. of 80% acetic acid for each 100 ml. of solution. Now the solution is heated to boiling, several drops of 3% hydrogen peroxide added to prevent reduction of the iron and then the iron precipitated with a 10% tannin solution with stirring. The filtered out, blue violet precipitate—the solution, or rather the filtrate must be yellowish brown—is dissolved in a little hot dilute sulfuric acid and this solution precipitated once again in the manner described above. The now beryllium-free precipitate is washed free from acid with water containing ammonium nitrate, dried and carefully ashed in a porcelain crucible. After fuming with nitric acid, the precipitate is transposed into Fe_2O_3 by strong ignition.

In the filtrate, the beryllium is determined after adding an excess of ammonia.

The separation of beryllium from chromium (50) can be done in the same way.

3. Separation of Beryllium from Titanium (50)

The solution, which contains titanium (IV) sulfate and ferric sulfate is neutralized with ammonia. Now 16 g. of ammonium acetate, 20 g. ammonium nitrate and 20–25 ml. of 80% acetic acid are added and the solution heated to boiling. The titanium is now precipitated with 10% tannin solution under stirring (a tenfold excess of reagent over the TiO_2 present is used). The fiery red precipitate is washed with a 10% acetic acid solution to which some ammonium nitrate has been added, dried and ashed. The residue is fumed with a little nitric acid and ignited to TiO_2.

The beryllium in the filtrate is best determined by precipitating as $Be(OH)_2$—tannin: The filtrate is heated to boiling with an excess of ammonium nitrate (the addition of an electrolyte accelerates the precipitation), an excess of 10% tannin solution added and the precipitation completed by adding ammonia drop by drop. The precipitate is filtered through a quantitative filter, washed with hot water, dried at 110–130° and changed into BeO through ignition in a quartz crucible and fuming with some nitric acid.

4. Separation of Beryllium from Zirconium (50)

The pure white zirconium-tannin compound is insoluble in acetic acid and in dilute hydrochloric (1:20). Out of zirconium salt solutions which are still completely clear and which, therefore, have not hydrolyzed so far that $Zr(OH)_4$ is precipitated, the zirconium-adsorption compound is formed a little at a time during the boiling of the solution. Exactly the same procedure is used here as in the separation of beryllium from titanium. The separation of beryllium from zirconium is quantitative with one precipitation.

5. Separation of Beryllium from Thorium (50)

The fine flocculent, white precipitant which colloidal thorium hydroxide forms with tannin is insoluble in 2–2.5% acetic acid in the presence of ammonium acetate. The thorium complex is freed from beryllium only by double precipitation. The precipitation is carried out in the same way as the separation of beryllium from iron.

Instead of igniting the thorium precipitate to the oxide in the presence of relatively small amounts of thorium the precipitate is dissolved in nitric acid and the organic substances destroyed by fuming with nitric acid. The thorium is now changed to the nitrate and can be determined as thorium picrolonate according to the method of Hecht and Ehrmann (63) described on page 45.

6. Separation of Beryllium from Tungsten (50)

The deep brown flocculent adsorption complex which is precipitated from an acidified alkali tungstate solution by tannin in the presence of an electrolyte is coagulated and made easily filterable by boiling for a considerable period. Small amounts of tungsten are precipitated by considerable boiling; with larger amounts of tungsten, traces of precipitate go into solution and the solution must stand for many hours on the water bath before they again precipitate.

Separation procedure: 30-50 g. of ammonium nitrate and 10 ml. of sulfuric acid are added to the neutral or alkaline solution of the alkali tungstate and the beryllium and the volume adjusted to from 300–500 ml. To the solution heated to boiling, a 10% tannin solution in about

10 fold excess (in relation to WO_3) is added and the solution kept boiling for about 5 minutes. Now 10 g. more ammonium nitrate are added and the solution boiled 5 minutes more whereby the brown adsorption compound precipitates in a heavy, easily filterable form. The filtered out precipitate is washed with dilute sulfuric acid (1:10) to which some ammonium nitrate has been added. With fairly large amounts of tungsten the filtrate should stand several hours on a boiling water bath, then the small precipitate is filtered through a small filter and washed with the above wash solution. The purified and dried precipitate is ashed in a porcelain crucible, smoked once with nitric acid and after strong ignition weighed as WO_3.

In the filtrate, the beryllium is determined as the pyrophosphate. Since correct results for this determination are possible only if the beryllium is precipitated as pure $BeNH_4PO_4 \cdot xH_2O$, the procedure of Moser and Singer (50, p. 679) is followed.

5 g. of ammonium phosphate, 20 g. of ammonium nitrate and 30 ml. of a cold saturated ammonium acetate solution are added to the weakly acid solution of the beryllium salt (nitrate or sulphate). The solution is heated to boiling and the precipitate is dissolved by pipetting in the necessary amount of nitric acid (1:2). (To avoid boiling over, the acid is best added through a rubber stopper with a hole in it.) Now 2.5% ammonia is slowly added from a burette (5-6 drops per minute) whereby a finely crystalline precipitate of $BeNH_4PO_4$ is slowly formed. When no more precipitate comes down on the addition of another drop of ammonia, sufficient ammonia is rapidly added to make the solution smell distinctly ammoniacal. After cooling, the solution is diluted with water and 25% ammonia added to it until the solution reacts alkaline to phenolphthalein. After the precipitate has completely settled it is filtered through a porcelain filter crucible and washed with hot, 5% ammonium nitrate solution until the filtrate no longer gives a phosphate test. The precipitate is ignited in an electric furnace to constant weight and the pure white $Be_2P_2O_7$ weighed.

$F = 0.0947; \log F = 8.97609-10.$

7. *Separation of Beryllium from Vanadium* (50)

Vanadium is precipitated out of alkali vanadate solutions in the presence of acetic acid as a deep blue, voluminous precipitate which is practically insoluble in acetic acid but soluble in mineral acids. (Here the tannin reduces a part of the V_2O_5 to V_2O_4.) Although the filtrate always has a greenish tint, no vanadium can be detected by the known reagents.

Separation procedure: 20 g. of ammonium acetate, 30 g. of ammonium nitrate and 2.5 ml. of 80% acetic acid for each 100 ml. of solution are added to the solution of alkali vanadate and beryllium salt diluted to 400–500 ml. The solution is now heated to boiling, precipitated with about a 10 fold excess of 10% tannin (in relation to V_2O_5) and boiled for several minutes more. The precipitate is filtered hot, washed with 10% ammonium acetate solution and ashed in a porcelain crucible. After fuming with nitric acid the residue is ignited until it melts and weighed as V_2O_5.

8. Determination of Gallium. Its Separation from Zinc, Cadmium, Cobalt, Nickel, Manganese, Beryllium and Thallium (51)

Gallium is precipitated according to the following procedure: Ammonium nitrate is added to the weakly acetic acid solution of Ga (III) salts (not more than 0.1 g. Ga_2O_3 should be present) until a content of about 2% is present. Now the solution is heated to boiling and a 10% solution of tannin added until precipitation is complete. The precipitate is filtered through a black band filter, washed with hot water to which some ammonium nitrate and several drops of acetic acid have been added, dried and ignited in a porcelain or quartz crucible to constant weight.

a. Separation of gallium from zinc (51): The solution of both metals is nearly neutralized with ammonia and then enough ammonium acetate added so that there is about 1% acetic acid in the solution.* 2 g. of ammonium nitrate for each 100 ml. of solution are added, the solution heated to boiling and precipitated with a 10% tannin solution. The precipitate is filtered, washed with hot water containing ammonium nitrate and acetic acid, dissolved in dilute hydrochloric acid and the solution reprecipitated.

The zinc in the filtrate is best determined by precipitation as the sulfide.

With this same procedure, gallium can be separated from zinc, cobalt, nickel and manganese. In all these separations, it is advisable to dissolve the precipitate in acid and to repeat the precipitation with tannin. In the filtrate, the other ions present can be determined after removing the organic material by fuming with nitric acid. The use of nitrosonaphthol (see p. 108) is recommended for the determination of cobalt; manganese can be precipitated as the sulfide.

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* An exact procedure as to how the solution is adjusted to a 1% acetic acid concentration is not given in the original paper.

b. The separation of gallium from beryllium (*51*): The gallium is precipitated with tannin as announced for zinc and the beryllium in the filtrate can also be determined as an adsorption compound by adding ammonia according to the procedure given on page 176.

c. The determination of uranium (*205*): 2 ml. of a 2% tannin solution are added to the uranyl salt solution for each 0.012 g. U present whereby the solution becomes dark brown in color. The solution is now heated to boiling for a short time and then a 10% ammoniacal ammonium acetate solution is added until a voluminous, chocolate brown precipitate comes down. The beaker is allowed to stand for some time on the water bath until the precipitate has settled to the bottom and then filtered through a black band filter. The precipitate is washed with hot water to which ammonium acetate and some ammonia have been added and after drying, it is ignited to U_3O_8.

The results obtained by this procedure are very exact.

d. The separation of gallium from thallium (*51*): The gallium is precipitated in the usual way with tannin. Before determining the thallium in the filtrate, the organic substance must first be removed—evaporation with concentrated nitric acid is best for this purpose. Then the thallium (III) salts are reduced to thallium (I) salts with sulfurous acid, sufficient alcohol added so that 10% by volume is present and the thallium precipitated as thallium (I) chromate (175).

e. Separation of tantalum from niobium (*48*): Powell and Schoeller (48, p. 226) give the following procedure: The exactly weighed oxide mixture (0.25–0.50 g.) is fused with 3–6 g. of dehydrated potassium pyrosulfate in a quartz crucible. The more niobium that is present, the larger the sample must be. If the mixture contains more than 0.25 g. of tantalum oxide, then the precipitate is so voluminous that it can scarcely be collected on a 12.5 cm. filter. If the melt should not be clear, then 0.5–1.0 ml. of sulfuric acid is added and the fusion repeated. If during the heating an easily attacked (corroded) oxide mixture yellow in color is formed, then niobium predominates; in the reverse case, tantalum predominates.

The cold melt is boiled with a saturated solution of 2–4 g. of ammonium oxalate and at the same time any clumps are broken up with a glass rod. If the niobic and tantalic acids go into solution with difficulty (high tantalum content) which is mostly due to the excessive liberation of SO_3 during the fusion, then the dissolving action is accelerated by adding several drops of dilute sulfuric acid.

This treatment usually gives clear solutions without residue; if this should not be the case, the solution is filtered into a 500 ml. beaker and the residue washed with hot water. The paper and the residue are ignited and again fused with some pyrosulfate. The melt is now dissolved in the ammonium oxalate solution and added to the main solution. This is now filtered to remove any residue (such as small amounts of silicic acid, calcium oxalate).

The solution now contains all of the tantalum and niobium as oxalic acid complexes and also a small amount of free oxalic acid (or acid oxalate); this varies with the acidity of the melt at the finish of the fusion. The most favorable acid concentration depends on the relative amount of both metals present.

First the acid concentration is adjusted: The solution which should contain about 0.1 g. of the tantalic and niobic acids in 100–150 ml. is heated to boiling and 10 ml. of a freshly prepared 2% tannin solution added to it. Practically always a lasting turbidity or a precipitate is formed during the boiling. If the solution should remain clear, then 0.5N ammonia is added from a burette until a lasting turbidity arises. (During this operation the tannic acid acts as an indicator; the formation of a turbid solution shows that the desired hydrogen ion concentration is present.) From the color of the precipitate, the approximate ratio of both metals can be estimated: If the precipitate is orange to red, then niobium is present in excess. If on the other hand, it has a sulfur yellow color, then the oxide mixture is at least one-third tantalum oxide. From the color of the precipitate the amount of tannin which must still be added can be estimated. For small portions of tantalum oxide, approximately a ten fold excess of tannin is used; but always at least 0.2 g. tannin is necessary. For larger amounts, the following table shows the necessary additions:

0.2 g. tannin for less than 0.03 g. Ta_2O_5
0.3–0.4 g. tannin for less than 0.03–0.06 g. Ta_2O_5
0.5–0.6 g. tannin for less than 0.06–0.12 g. Ta_2O_5
0.7–0.8 g. tannin for less than 0.12–0.18 g. Ta_2O_5
0.9–1.0 g. tannin for less than 0.18–0.25 g. Ta_2O_5

Finally 5 g. of ammonium chloride in a saturated solution is added to the boiling solution and after precipitation starts the solution is boiled 10–15 minutes more. The precipitate (N_1) is now either orange to red (Method A) or it is sulfur yellow (Method B).

METHOD A

By correct work the precipitate is completely coagulated and settled and the solution is free from all color (orange) or turbidity (a straw yellow color tone is often present in the solution but is unimportant). If this is not the case, the boiling must be continued and 0.5N ammonia added until the above conditions are fulfilled.

The precipitate is collected on a black band filter and washed with a 2% ammonium chloride solution. The clear and colorless (or straw yellow) filtrate is boiled again and 5–10 ml. of the tannin solution added to it whereby an orange to red colloidal solution again is formed. By adding 0.5N ammonia drop by drop, the solution is decolorized and the precipitate (N_1a) thrown down. The solution is digested for some time on the water bath and allowed to stand over night. On the next day the precipitate is filtered off and washed with 2% ammonium chloride solution. The precipitates N_1 and N_1a are ashed in a quartz crucible and the ignited oxide mixture weighed. They are then fused again and treated exactly as described on page 181, only instead of Method A, one uses—

METHOD B

The precipitate is allowed to settle, the hot solution together with the precipitate poured through a black band filter and the precipitate washed with a 2% ammonium chloride solution. When the precipitate is removed from the beaker except some small traces, the filtrate is poured back into the original beaker and evaporated to about three-fourths of the original volume. Now the wash solution which was separated before and several milliliters of tannin solution are added to the boiling filtrate and the solution slowly titrated with 0.5N ammonia (see p. 181) until the orange red color disappears. Saturated ammonium oxalate solution is now added in portions of 10–25 ml. until the yellow precipitate begins to coagulate and the supernatant liquid is clear and colorless. In order that the solution be completely clear, it is kept on the water bath for some time and then allowed to stand overnight. The precipitate is now filtered from the clear solution and treated as described under Method A. Both precipitates are combined, ashed in a quartz crucible and weighed as Ta_2O_5 after strong ignition.

The filtrate from the second precipitation which should not be yellow (at most it may have a faint yellowish tinge) is tested for completeness of precipitation by repeating the above described ammonia-ammonium oxalate treatment. If a small amount of tantalum should be present, then the yellow precipitate (N_1b) is filtered out, ignited and the weight added to the main ignition product.

If, however, the precipitate has an orange red color then the separation was complete.

METHOD C

If both elements are present in nearly the same amount, then a combination of Method A and Method B can be used.

The procedure depends on the precipitation of the main part of the tantalum as the niobium free, sulfur yellow precipitate, N_1, which is ignited and weighed. The rest of the tantalum is now precipitated with niobium as an orange colored precipitate, N_1a, which is ignited and obtained in the pure form as N_2 according to Method B.

In cases where the addition of 0.2 g. of tannin colors the boiling solution orange, then 1N sulfuric acid is added dropwise until a pure yellow color appears. Now the rest of the tannin and the ammonium chloride is added. The yellow precipitate is collected, ignited and weighed. Nothing further has to be done with this precipitate. The boiling filtrate is titrated with 0.5N ammonia and the orange red precipitate which is formed is collected, ignited and purified according to Method B.

The advantage of this method is that most of the tantalum is precipitated in the pure form. The fusion of the smaller precipitate, N_1, is more easily carried out and by working with a smaller volume the errors caused by incomplete precipitation of the tantalum and coprecipitation of the niobium are avoided.

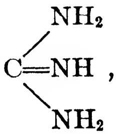
The niobium is determined indirectly by subtracting the weight of the Ta_2O_5 from the sum of the oxides. The direct determination of niobium has no particular advantage.

The Bureau of Standards has checked this method and recommends that it replace the older methods (compare to (48, p. 232) (53)).

Finally there is still one reagent to be discussed which does not fit into any of the groups but which has a certain amount of value as a specific reagent.

E. GUANIDINE CARBONATE (206)

$(CH_6N_3)_2CO_3$, M.P. 197°

Guanidine,  $C\begin{array}{l} \diagup NH_2 \\ {=}NH \\ \diagdown NH_2 \end{array}$, is a strong, mono-acid base whose aqueous solution is nearly as strong as that of sodium hydroxide.

The effect of guanidine carbonate as reagent depends therefore on the alkaline reaction of the aqueous solution.

The reagent reacts differently with aluminum and beryllium compounds so it can be used to separate the two elements.

Guanidine forms a white precipitate with aluminum which is soluble in an excess of the precipitant. Ammonium tartrate prevents the precipitation.

The reagent also forms a precipitate with beryllium which is not soluble in an excess of the reagent. Ammonium acetate does not prevent the precipitation.

The composition of the beryllium precipitate depends very much on the precipitation conditions. Jílek and Kořa (207) have investigated the precipitate and suggest the following formula:

$$2BeCO_3 \cdot Be(OH)_2 \cdot xH_2O$$

Determination of beryllium and its separation from aluminum (207): 50 ml. of an ammonium tartrate solution obtained by neutralizing an aqueous solution containing 42.5 g. of tartaric acid with dilute ammonia and diluting to 2 liters is added to the weakly acid solution of beryllium chloride or sulfate. (Not more than 0.1 g. BeO or 0.1 g. Al_2O_3 should be present.) Now sufficient potassium hydroxide is added so that the solution is just acid to methyl red. Then with steady stirring 150 ml. of a 4% guanidine carbonate solution and 2.5 ml. of a nearly neutral 40% formaldehyde solution are added to the cold solution. When precipitation is complete, the solution is diluted to 250 ml. and allowed to stand over night.

The silk-like gleaming, crystalline precipitate is filtered through a blue band filter and washed with the following solution: 50 ml. of the ammonium acetate solution, 150 ml. 4% reagent solution and 2.5 ml. of 40% formaldehyde diluted to 250 ml. The precipitate is washed with this solution until it is free from chlorides or sulfates, then ashed wet and the beryllium oxide ignited to constant weight.

Since the precipitate is soluble in ammonium salts and in ammonium carbonate, the ammonium carbonate formed by the reaction of guanidine carbonate with ammonium tartrate must be removed. If only a little ammonium salt is present, then by adding formaldehyde the ammonium carbonate is changed into hexamethyltetramine. If the determination has to be done in the presence of unknown ammonium salt concentration, then the following procedure is applicable: 50 ml. of ammonium tartrate solution and about 5 ml. of a 40% formaldehyde solution are added to the solution. The solution is now made just alkaline to phenolphthalein with 3 N sodium hydroxide. (The red color should not disappear when more formaldehyde is added.) After this dilute hydrochloric acid is added until the solution is acid to methyl red and then the excess acid is buffered with sodium hydroxide until the solution is just acid to methyl red. Then the above procedure may be followed.

If more than 1 g. of precipitant for a volume of 100 ml. and a maximum content of 0.1 g. BeO is used, then in the cold, a finely-crystalline gleaming precipitate comes down (see page 184). By strong dilution or by washing with hot 1% ammonium nitrate solution, the precipitate loses its luster and becomes flocculent. The filtrate also is a little turbid.

The crystalline precipitate is somewhat soluble in cold water and in cold 1% ammonium nitrate solution. By heating, the crystalline precipitate hydrolyzes to a flocculent form which is practically insoluble in hot 1% ammonium nitrate solution.

With this method beryllium can be quantitatively determined in the presence of aluminum (not more than 0.1 g. BeO and 0.1 g. Al_2O_3) and also 0.5 g. of ammonium chloride as well as in the presence of potassium and sodium chlorides.

Using the same procedure, beryllium can be separated from iron, uranium, thorium, thallium, chromate, molybdate, copper, arsenite and antimonite (207).

The determination of beryllium in the presence of vanadium (207): Since the beryllium and vanadium salt solution to which ammonium acetate has been added contains free VO_4''' ions (as shown by the yellow color of the solution) it is partially precipitated as a yellow precipitate by the addition of guanidine carbonate. This is prevented first by adding a base to the acid solution until the yellow color disappears. Now dilute hydrochloric acid is added until the solution is just acid to methyl red and the beryllium precipitated with guanidine carbonate.

The beryllium results are very good.

In the same way, beryllium can be separated from tungstic acid with good results.

In conclusion a few additional reagents are listed below which may be useful for certain special determinations:

1. **Hexamethylenetetramine.** A. Hemmeler, *Z. anal. Chem.*, **110**, 426 (1937): "Determination of copper with hexamethylenetetramine." T. Akiyama, *J. pharmac. Soc. Japan*, **57**, 19; C. 1937, II, 444: "Quantitative determination of beryllium with hexamethylenetetramine." J. Dick, *Z. anal. Chem.*, **111**, 260, (1938): "A new procedure for the determination of copper (precipitation of copper as urotropine-benzoate complex)."

2. **Phenylthiohydantoic acid.** H. D. Hall, Diss. U. of Michigan, 1920: "The separation of cobalt and copper from other metals by phenylthiohydantoic

acid and the volumetric determination of cobalt." See also the work of Willard and Hall, *J. Am. Chem. Soc.*, **44,** 2219, 2226, 2237, 2253 (1923).

3. **Chromium-en-chloride.** $(Cren_3)Cl_3 \cdot 3 \cdot 5H_2O$. G. Spacu and A. Pop, *Z. anal. Chem.*, **111,** 254 (1938): "A new gravimetric, semi-micro method for determining antimony."

4. **9-methyl-2,3,7-trioxy-6-fluorenone.** Duckert, *Helv. Chim. Acta,* **20,** 362 (1937): "9-methyl-2,3,7-trioxy-6-fluorenone as a specific reagent for antimony." Ph. Wenger, Duckert, Blancrain, *Helv. Chim. Acta,* **20,** 1427 (1937): "9-methyl-2,3,7-trioxy-6-fluorenone as a specific reagent for antimony."

5. **2-Nitroso-1-naphthol-4-sulfonic acid.** L. A. Sarver, *Ind. Eng. Chem.*, Analyt. Ed., **10,** 378 (1938). "Detection of cobalt, copper and iron (II) with 2-nitroso-1-naphthol-4-sulfonic acid."

6. **Rubeanic acid.** H. Woelbling, B. Steiger, *Mikrochemie,* **15** (N.F. 9), 315 (1934): "Rubeanic acid as a reagent for the elements of the platinum group."

7. **Dilituric acid** (5-nitro-barbituric acid). H. Fredholm, *Z. anal. Chem.*, **104,** 400 (1936): "A sensitive reaction for detecting potassium."

8. **m-nitrobenzoic acid.** A. C. Neish, *J. Am. Chem. Soc.*, **26,** 780 (1904): "A new separation of thorium from cerium, lanthanum and didymium with m-nitrobenzoic acid." A. Kolb, H. Ahrle, *Z. angew. Chem.* **18,** 92 (1905): Application of organic acids for separating thorium dioxide from cerium-, lanthanum- and didymium oxide.

9. **Ammonium salicylate.** M. Dittrich, S. Freund, *Z. anorg. allgem. Chem.*, **56,** 344 (1907): "A new separation of titanium from zirconium (page 346). Separation of titanium and thorium (page 348). Separation thorium, titanium and zirconium from iron."

10. **p-oxyphenylarsenic acid.** C. T. Simpson, G. C. Chandar, *Ind. Eng. Chem.*, Anal. Ed., **10,** 642 (1938): "$HO \cdot C_6H_4 \cdot AsO_3H$ as a reagent for the detection of titanium and zinc."

BIBLIOGRAPHY

(1) P. Pfeiffer, "Organische Molekülverbindungen," 2nd ed., Stuttgart, 1927.

(2) P. Pfeiffer, *Ber.*, **63,** 1811 (1930).

(3) O. Wallach, *Ann.*, **437,** 148 (1924). Further information is to be found in F. Feigl's "Qualitative Analysis by Spot Tests," 2nd Engl. Ed., N. Y., 1939.

(4) A. Werner, "Neure Anschauungen auf dem Gebiete der anorganischen Chemie," Braunschweig, 19—.

(5) Compare B. W. Schlenk and E. Bergmann, "Ausführliches Lehrbuch der organischen Chemie," Leipzig and Wien, 1932.
V. Meyer and P. Jacobson, "Lehrbuch der organischen Chemie," Book I, Part I, page 808; Book II, Part I, page 771.

(6) H. Funk and M. Ditt, *Z. anal. Chem.*, **91,** 332 (1933) (zinc, cadmium, separation of these metals from the alkali earths); *Z. anal. Chem.*, **93,** 241 (1933) (cobalt, nickel, copper); Funk and Demmel, *Z. anal. Chem.*, **96,** 385 (1934) (manganese).

(7) L. Hugounenq, G. Florence and E. Couture, *Bull. Soc. chim. biol.*, **7,** 58 (1925).

(8) J. Kisser, *Mikrochemie,* **1,** 25 (1923) (calcium in micro and histological chemistry analysis).

(9) R. Dworzak and W. Reich-Rohrwig, *Z. anal. Chem.*, **86,** 98 (1931) (calcium).

(10) M. Busch, *Ber.*, **38,** 861 (1905) (nitric acid).

(11) M. Gutbier, *Z. angew. Chem.*, **18,** 494 (1905) (nitric acid).

(12) W. Geilmann and A. Voigt, *Z. anorg. allgem. Chem.*, **193,** 311 (1930) (soluble perrhenates).

(13) L. Tschugaeff, *Ber.*, **38,** 2520 (1905) (nickel).

(14) O. Brunck, *Z. angew. Chem.*, **20,** 1844 (1907) (nickel, its separation from the other metals of the ammonium sulfide group).

(15) R. Strebinger, *Oesterr. Chem.-Ztg.*, **21,** 71 (1918): "Proposed quantitative determination of ions in a micro analytical manner." Compare also E. Kroupa, *Mikrochim. Acta,* **3,** 306 (1938) (nickel and uranium).

(16) P. R. Rây and M. K. Bose, *Z. anal. Chem.*, **95,** 400 (1933) (copper, zinc, cadmium, uranium; colorimetric determination of iron).

(17) F. Feigl, *Ber.*, **56,** 2083 (1923) (copper). Compare also F. Feigl, G. Sicher, O. Singer, *Ber.*, **58,** 2294 (1925).

(18) F. Ephraim, *Ber.*, **63,** 1928 (1930) (copper).

(19) F. Ephraim, *Ber.*, **64,** 1210 (1931).

(20) F. Ephraim, *Ber.*, **64,** 1215 (1931) (structure).

(21) F. Feigl and A. Bondi, *Ber.*, **64,** 2819 (1931) (structure).

(22) F. Feigl and A. Christiani-Kronwald, *Z. anal. Chem.*, **65,** 341 (1924) (nickel).

(23) O. Baudisch, *Chem.-Ztg.*, **33**, 1298 (1909) (separations).

(24) R. Berg and O. Roebling, *Ber.*, **68**, 403 (1935).

(25) R. Berg and O. Roebling, *Angew. Chem.*, **48**, 430 (1935).

(26) M. Ilinski, *Ber.*, **17**, 2592 (1884); M. Ilinski and G. v. Knorre, *Ber.*, **18**, 699 (1885) (separation of cobalt and nickel).

(27) C. Mayr and F. Feigl, *Z. anal. Chem.*, **90**, 15 (1932) (determination and separation of cobalt).

(28) G. Spacu and M. Kuraš, *Z. anal. Chem.*, **102**, 24 (1935). Compare also M. Kuraš, *Chem. obzor*, **13**, 95; C. **1938**, II, 1998 (cations).

(29) L. Springer, Dissertation, Techn. Hochschule Muenchen, **1913**, p. 32.

(30) F. Feigl, *Z. anal. Chem.*, **64**, 41 (1924) (antimony).

(31) F. Feigl and H. Ordelt, *Z. anal. Chem.*, **65**, 448 (1924) (bismuth and its separation from lead).

(32) S. Hilpert and L. Wolf, *Ber.*, **46**, 2215 (1913) (aromatic hydrocarbons).

(33) Hellmut Fischer, *Wiss. Veröffentl. Siemens-Konzern*, **4**, 158 (1925); C. **1926**, II, 620.

(34) H. Fischer, *Angew. Chem.*, **47**, 685 (1934).

(35) Moser and E. Iranýi, *Mh. Chem.*, **44**, 91 (1923) (separation of titanium from iron and aluminum).

(36) L. Moser, *Monatsh.*, **44**, 91 (1923) (separation of uranium from titanium, iron and aluminum).

(37) L. Moser and A. Brukl, *Ber.*, **58**, I, 380 (1925) (separation of iron and aluminum from manganese and magnesium as well as phosphorus).

(38) Ph. Horkheimer, *Pharm. Ztg.*, **80**, 660 (1935).

(39) R. Berg and O. Wurm, *Ber.*, **60**, 1664 (1927): Concerning the salts of the halogen acids of cadmium and bismuth with organic bases and their analytical value.

(40) G. Spacu and G. Suciu, *Z. anal. Chem.*, **77**, 334 (1929) (mercury).

(41) G. Spacu and P. Spacu, *Z. anal. Chem.*, **80**, 187 (1932) (mercury).

(42) G. Spacu and P. Spacu, *Z. anal. Chem.*, **90**, 182 (1932) (macro and micro analytical silver determination).

(43) G. Spacu, *Bulet. Societ. de Stiinte din Cluj*, **1**, 348; C. **1923**, II, 508 (zinc).
G. Spacu, *Bulet. Societ. de Stiinte din Cluj*, **1**, 348; C. **1923**, II, 1052 (zinc).
G. Spacu and R. Ripan, *Bulet. Societ. de Stiinte din Cluj*, **1**, 314; C. **1923**, II, 380 (nickel).
G. Spacu, *Bulet. Societ. de Stiinte din Cluj*, **1**, 538; C. **1923**, IV, 187 (cadmium).

(44) G. Spacu and G. Macarovici, *Z. anal. Chem.*, **102**, 350 (1935) (copper).

(45) C. Mahr, *Angew. Chem.*, **50**, 412 (1937).

(46) C. Mahr and H. Ohle, *Z. anal. Chem.*, **109**, 1 (1937) (determination and separation of Cd from Zn).

(47) C. Mahr and H. Ohle, *Z. anorg. allg. Chem.*, **234**, 224 (1937) (lead in presence of other metals).

(48) A. R. Powell and W. R. Schoeller, *Analyst*, **50**, 485 (1925); also *Z. anorg. allgem. Chem.*, **151**, 221 (1926) (separation of tantalum from niobium; the detection and estimation of small amounts of tantalum in niobium compounds).

(49) L. Moser and M. Niessner, *Monatsh.*, **48**, 113 (1927) (quantitative separation of beryllium from aluminum).

(50) L. MOSER AND J. SINGER, *Monatsh.*, **48**, 673 (1927) (beryllium and the dependent separations).

(51) L. MOSER AND A. BRUKL, *Monatsh.*, **50**, 181 (1928) (gallium).

(52) Concerning the adsorption compounds compare: J. M. VAN BEMMELEN, *Z. anorg. allgem. Chem.*, **23**, 321 (1900).

W. BILTZ, *Ber.*, **37**, 1905 (1904).

More recent work is published in H. FREUNDLICH, "Fortschritte der Kolloidchemie," Dresden and Leipzig, 1926. See page 57, the section titled "Dehydratisierender Einfluss des Tannins auf hydrophile Sole."

(53) W. R. SCHOELLER, "The Analytical Chemistry of Tantalum and Niobium," London and New York, 1937.

(54) CH. CIMERMAN AND P. WENGER, *Mikrochemie* (N.F.), **18**, 1 (1935) (zinc).

(55) G. CHEVALIER, *Prog. agric. vitic.*, **97**, 354 (1932): Recommends 40 mg. methyl red, 80 mg. bromthymol blue, 80 mg. phenolphthalein, 2 ml. 0.1N Na_2CO_3, dissolved in 50 ml. alcohol (95%) and 50 ml. of water.

(56) W. PRODINGER, unpublished determinations.

(57) C. MAYR, *Z. anal. Chem.*, **92**, 166 (1933).

(58) P. WENGER, CH. CIMERMAN, A. CORBAZ, *Mikrochim. Acta*, **2**, 314 (1937).

P. WENGER, CH. CIMERMAN, A. CORBAZ, *Compt. rend. soc. phys. hist. nat. Genève*, **1937**, 156, 160.

(59) H. FUNK AND RÖMER, *Z. anal. Chem.*, **101**, 85 (1935).

(60) H. ALTEN, H. WEILAND AND E. KNIPPENBERG, *Biochem. Z.*, **265**, 85 (1933).

(61) F. HECHT, W. REICH-ROHRWIG AND H. BRANTNER, *Z. anal. Chem.*, **95**, 152 (1933).

(62) W. REICH-ROHRWIG, *Mikrochemie* (N.F.), **12**, 189 (1932).

(63) F. HECHT AND W. EHRMANN, *Z. anal. Chem.*, **100**, 87 (1935).

(64) L. W. WINKLER, *Z. Angew. Chem.*, **34**, 46 (1921).

(65) A. C. RICE, H. C. FOGGS, C. JAMES, *J. Am. Chem. Soc.*, **48**, 895 (1926) (zirconium and thorium).

(66) P. KLINGER, O. SCHLIESSMANN, *Arch. Eisenhüttenw.*, **7**, 113 (1933); C. **1933**, II, 2564.

(67) J. S. KNAPPER, K. A. CRAIG AND G. C. CHANDLER, *J. Am. Chem. Soc.*, **55**, 3945 (1933).

(68) F. FEIGL, *Ber.*, **57**, 758 (1924).

(69) M. A. ROLLET, *Compt. Rend.*, **193**, II, 212 (1926).

(70) N. STRAFFORD, *Analyst*, **61**, 170 (1936).

(71) M. WUNDER, V. THÜRINGER, *Z. anal. Chem.*, **52**, 101 (1913).

(72) M. WUNDER, V. THÜRINGER, *Ann. chim. anal. chim. appl.*, **17**, 201; C. **1912**, II, 550.

(73) M. WUNDER, V. THÜRINGER, *Z. anal. Chem.*, **52**, 660 (1913).

(74) A. M. SANKO AND G. A. BUTENKO, *Betriebslab.* (Russ.), **6**, 545 (1937); C. **1938**, II, 128.

(75) P. R. RÂY AND M. K. BOSE, *Mikrochemie* (N.F.), **17**, 11 (1935).

(76) P. R. RÂY AND R. GUPTA, *Mikrochemie* (N.F.), **17**, 14 (1935).

(77) P. R. RÂY AND A. K. MAJUNDAR, *Z. anal. Chem.*, **100**, 324 (1935).

(78) RÂY AND GUPTA, *Mikrochemie* (N.F.), **17**, 14 (1935).

(79) RÂY AND BOSE, *Mikrochemie* (N.F.), **18**, 89.

(80) H. A. KAR, *Ind. Eng. Chem.*, Anal. Ed., **7**, 193 (1935).

(81) R. Strebinger, *Mikrochemie,* **1,** 72 (1923).
R. Strebinger and J. Pollack, *Mikrochemie,* **2,** 125 (1924).
(82) F. Hecht and R. Reissner, *Mikrochemie* (N.F.), **17,** 130 (1935).
(83) H. B. Knowles, *Bur. Standards J. Research,* **9,** 1–7 (1932).
(84) S. Astin and H. L. Riley, *J. Chem. Soc.,* **1933,** 34 (copper).
(85) H. Alten, H. Wandrowsky and E. Knippenberg, *Mikrochemie* (N.F.), **14, 77** (1936).
(86) H. Holzer, *Z. anal. Chemie,* **95,** 932 (1933).
(87) I. Ubaldini, *Chimica e industria* (Italy), **19,** 65; C. **1937,** I, 3680 (1937).
(88) H. L. Riley, *J. chem. Soc.,* **1933,** 895.
(89) M. Ishibashi and H. Kishi, *Bull. Chem. Soc. Japan,* **10,** 362 (1935); C. **1935,** II, 3953.
(90) E. Fischer, *Ber.,* **22,** 1931 (1889).
(91) W. Zinkeisen: *Ber.,* **22,** 2946 (1889). See p. 2952.
(92) H. Biltz and O. Hödtke, *Z. anorg. allgem. Chem.,* **66,** 426 (1910).
(93) H. Nissenson, *Z. Angew. Chem.,* **23,** 969 (1910).
(94) J. Hanuš and A. Soukoup, *Z. anorg. allgem. Chem.,* **68,** 52 (1910).
(95) A. Pinkus and E. Belche, *Bull. Soc. chim. Belg.,* **36,** 277; C. **1927,** II, 1056.
(96) W. M. Thornton, Jr., *Z. anorg. allgem. Chem.,* **87,** 375 (1914).
(97) E. Schwarz von Bergkampf, *Z. anal. Chem.,* **83,** 345 (1931).
(98) C. Mayr and A. Gebauer, *Z. anal. Chem.,* **113,** 189 (1938).
(99) A. Angeletti, *Ann. chim. applicata,* **17,** 53; C. **1927,** II, 719.
(100) L. Silverman, *Chemist-Analyst,* **23,** Nr. 3, 4 (1934).
(101) W. R. Bennett, *J. Am. Chem. Soc.,* **56,** 277 (1934).
(102) A. Pinkus and J. Dernies, *Bull. Soc. Chem. Belg.,* **37,** 267; C. **1928,** II, 2670.
(103) L. Moser and A. Brukl, *Monatsh. Chem.,* **51,** 325 (1929).
(104) E. Schwarz von Bergkampf, *Z. anal. Chem.,* **90,** 333 (1932).
(105) H. Pied, *Compt. rend.,* **179,** 897 (1924).
(106) J. Brown, *J. Am. Chem. Soc.,* **39,** 2358 (1917).
(107) W. M. Thornton, Jr., *Chem. News,* **114,** 13 (1916).
(108) N. J. Matwejew, *Chem. Journ.,* Ser. B, *Journ. Angew. chem.* (russ), **4,** 275; C. **1932,** I, 978.
(109) A. Pinkus and M. Katzenstein, *Bull. Soc. Chem. Belg.,* **39,** 179; C. **1930,** II, 1889.
(110) S. G. Clarke, *Analyst,* **52,** 466 (1927).
(111) N. I. Ssurenkow, *Betriebslab,* **1933,** 17; C. **1935,** I, 2415.
(112) N. J. Matwejew, *Tsretnye Metal.* (Non-ferrous Metals), **1930,** 85; C. **1930,** I, 3813.
(113) K. Schröder, *Z. anorg. allgem. Chem.,* **72,** 89 (1911).
(114) A. Pinkus and J. Claessens, *Bull. Soc. Chim. Belg.,* **36,** 413; C. **27,** II, 1872.
(115) N. H. Furman, *Ind. Eng. Chem.,* **15,** 1071 (1924).
(116) W. M. Thornton, Jr., and E. M. Hayden, *Z. anorg. allgem. Chem.,* **89,** **377** (1914).
(117) G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.,* **12,** 344 (1920).
(117a) Baudisch and Holmes, *Z. analyt. Chem.,* **119,** 16 (1940); see also the booklet *Cupferron and Neocupferron,* published by the G. Fredrick Smith Chemical Co.
(118) R. Berg and O. Röbling, *Angew. Chem.,* **48,** 597 (1935).

(119) R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **112**, 162 (1938).

(120) R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **109**, 305 (1937).

(121) R. Berg, E. S. Fahrenkamp and W. Roebling, *Mikrochemie*, Molisch-Festschrift, **1936**, 42.

(122) R. Berg and E. S. Fahrenkamp, *Mikrochimica Acta*, **64** (1937).

(123) A. Craig, L. Cudroff, *Chemist-Analyst*, **24**, 10 (1935).

(124) W. Schmidt, *Z. anorg. allgem. Chem.*, **80**, 355 (1913).

(125) M. Wunder and V. Thüringer, *Z. anal. Chem.*, **52**, 737 (1913).

(126) R. Berg, *J. Prakt. Chem.*, **115**, 178 (1927); see also Fr. Hahn, *Z. angew. Chem.*, **39**, 1198 (1926); also Fr. Hahn and K. Vieweg, *Z. analyt. Chem.*, **71**, 122 (1927).

(127) R. Berg, *Z. angew. Chem.*, **41**, 611 (1928); S. Schukowskaja and S. Bernstein, *Zawodskaya Lab.*, **3**, 214 (1934).

(128) R. Berg, "Die analytische Verwendung von O-Oxyquinoline (Oxin) und seiner Derivate," F. Enke (1938), 2nd ed.; Die Chemische Analyse, XXXIV.

(129) Skraup, *Monatsh. Chem.*, **3**, 540 (1883); worked with oxine-metal compounds, using them chiefly in identification; see also Fox, *J. Am. Chem. Soc.*, **97**, I, 1119 (1910); Zetsche, Silberman and Vieli, *Helv. Chim. Acta*, **8**, 596 (1925)

(130) H. Goto, *J. Chem. Soc. Japan*, **54**, 725 (1933); also **56**, 314 (1935); see also K. Shiba, *Reports of Tokyo Imp. Res. Inst.*, **27** (1932).

(131) H. R. Fleck and A. M. Ward, *Analyst*, **58**, 3888 (1933); H. R. Fleck, *Analyst*, **62**, 378 (1937).

(132) R. Berg, *Pharm. Ztg.*, **71**, 1542 (1926).

(133) Bucherer and Meier, *Z. analyt. Chem.*, **82**, 14 (1930).

(134) Fr. L. Hahn and E. Hartleb, *Z. analyt. Chem.*, **71**, 225 (1927).

(135) P. Wenger, Ch. Cimerman and M. Wyszewienska, *Mikrochemie*, **18**, 182 (1935); F. Hecht, *Z. analyt. Chem.*, **110**, 391 (1937); W. A. Hough and J. B. Ficklen, *J. Am. Chem. Soc.*, **52**, 4752 (1930); R. Strebinger and W. Reiff, *Mikrochemie* (Pregl-Festschrift); A. Benedetti-Pichler, *Mikrochemie* (In both Pregl- and Emich-Festschrift).

(136) R. Berg, *Z. analyt. Chem.*, **71**, 171 (1927).

(137) M. E. Stas, *Z. analyt. Chem.*, **92**, 43 (1933).

(138) R. Berg, *Z. analyt. Chem.*, **76**, 202 (1929).

(139) R. Berg, *Z. analyt. Chem.*, **71**, 23 (1927).

(140) L. Moser and K. Schutt, *Monatsh. Chem.*, **51**, 975 (1929).

(141) J. Redmond and H. Bright, *Bureau of Standards, Jour. Research*, **6**, 113 (1931); see also J. Redmond, *B. S. Jour. Research*, **10**, 823 (1933).

(142) R. Berg, *Z. analyt. Chem.*, **71**, 369 (1927); see also G. E. F. Lundell and H. B. Knowles, *B. S. Jour. Research*, **3**, 91 (1929).

(143) R. Berg and M. Teitelbaum, *Z. analyt. Chem.*, **81**, 1 (1930).

(144) R. Lang and J. Reifer, *Z. analyt. Chem.*, **93**, 162 (1933).

(145) T. Heczko, *Chem. Ztg.*, **58**, 1032 (1934).

(146) R. Berg, *Z. analyt. Chem.*, **76**, 191 (1929).

(147) R. Berg, *Z. analyt. Chem.*, **70**, 341 (1927).

(148) J. M. Kolthoff and E. Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928); M. Niessner, *Z. analyt. Chem.*, **76**, 135 (1929).

(149) G. Spacu and M. Kuraš, *Z. anal. Chem.*, **102,** 108 (1935).
(150) G. Spacu and M. Kuraš, *Z. anal. Chem.*, **104,** 88 (1936).
(151) E. A. Ostroumov, *Z. anal. Chem.*, **106,** 36 (1936).
(152) Hellmut Fischer, G. Leopoldi and H. von Uslar, *Z. anal. Chem.*, **101,** 1 (1935).
(153) H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **103,** 241 (1935).
(154) See also: H. Woelbling and B. Steiger, *Angew. Chem.*, **46,** 279 (1933).
(155) H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107,** 241 (1936).
(156) H. Fischer and G. Leopoldi, *Metall. u. Erz.*, **35,** 86 (1938).
(157) P. L. Hibbard, *Ind. Eng. Chem.*, Anal. Ed., **9,** 127 (1937).
(158) D. A. Biddle, *Ind. Eng. Chem.*, Anal. Ed., **8,** 99 (1936).
(159) H. Fischer and G. Leopoldi, *Mikrochimica Acta*, **1,** 30 (1937).
(160) H. Fischer and G. Leopoldi, *Angew. Chem.*, **47,** 90 (1934).
(161) O. B. Winter, H. M. Robinson, F. W. Lamb and E. J. Miller, *Ind. Eng. Chem.*, Anal. Ed., **1,** 263 (1935).
(162) W. E. White, *Ind. Eng. Chem.*, Anal. Ed., **8,** 231 (1936).
(163) A. W. Jewlanowa, *J. angew. Chem.* (russ.), **9,** 1690 (1936); C. **1937,** I, 3028.
(164) L. Ellis, *Analyst*, **61,** 178 (1936).
(165) Herbert Müller, *Z. anal. Chem.*, **113,** 161 (1938).
(166) H. Grubitsch, J. Sinigoj, *Z. anal. Chem.*, **114,** 30 (1938).
(167) H. Fischer, *Angew. Chemie*, **50,** 919 (1937).
(168) E. B. Sandell, *Ind. Eng. Chem.*, Anal. Ed., **9,** 464 (1937).
(169) N. L. Allport, G. H. Skrimshire, *Analyst*, **57,** 440 (1932).
(170) J. Gangl, E. Liedl, *Mikrochemie*, Molisch-Festschrift, 147 (1936).
(171) K. Heller, *Mikrochemie*, **23,** 78 (1937).
(172) F. Rohner, *Helv. Chim. Acta*, **21,** 1 (1938).
(173) Compare: D. Balarew, *Z. anorg. allg. Chem.*, **97,** 149 (1915).
(174) L. Karaoglanow, C. **1912,** II, 547.
(175) L. Moser and A. Brukl, *Monatsh. Chem.*, **47,** 709 (1926).
(176) Compare: F. P. Treadwell, "*Quantitative Analysis,*" (p. 143).
(177) R. Lang, *Z. anorg. allg. Chem.*, **122,** 332 (1922).
(178) See also: Vol. 33 of "Chemische Analyse" on Iodomectric methods (page 66).
(179) R. Berg, *Z. anal. Chem.*, **69,** 342, 369 (1926).
(180) R. Berg, "Die Bestimmung der Metalle mit o-Oxychinolin," Stuttgart, 1938. Also ref. 155, page 69.
(181) F. Hecht and R. Reissner, *Z. anal. Chem.*, **103,** 88 (1935).
(182) R. Strebinger and G. Ortner, *Z. anal. Chem.*, **107,** 14 (1936).
(183) G. Spacu, *Bulet. Societ. de Stiinte din Cluj*, **1,** 284 (1927).
(184) G. Spacu and J. Dick, *Z. anal. Chem.*, **71,** 185 (1927).
(185) A. Tettamanzi, *Ind. Chimica*, **9,** 609; C. **1934,** II, 1811.
(186) G. Spacu and J. Dick, *Z. anal. Chem.*, **73,** 279 (1928).
(187) R. Ripan, *Bulet. Societ. de Stiinte din Cluj*, **2,** 211 (1924); C. **1924,** II, 2684.
(188) G. Spacu and J. Dick, *Z. anal. Chem.*, **72,** 289 (1927).
(189) G. Spacu and J. Dick, *Z. anal. Chem.*, **71,** 442 (1927).
(190) G. Spacu and J. Dick, *Z. anal. Chem.*, **71,** 97 (1927).
(191) G. Rotter, *Z. anal. Chem.*, **64,** 102 (1924).
(192) G. Spacu, *Z. anal. Chem.*, **67,** 147 (1926).
(193) G. Spacu, *Z. anal. Chem.*, **67,** 27 (1926).

(194) G. Spacu, *Bull. Soc. Chim. France,* (5) **3,** 1061 (19).

(195) A. Tettamanzi, *Atti accad. sci. Torino, Classe sci. fis. mat. nat.,* **69,** I, 197; C. **1935,** I, 115.

(196) W. Schlenk, *Ann. Chem.,* **363,** 313 (1908).

(197) G. Spacu and C. G. Macarovici, *Atti accad. sci. Torino, Classe sci. fis. mat. nat.,* **72**; C. **1937**, II, 3784: A new reaction of copper with benzidine and a new method for determining traces of copper.

(198) G. Spacu and P. Spacu, *Bul. soc. Stiinte din Cluj.,* **5,** 387; C. **1931,** I, 1425.

(199) M. Straumanis and A. Cirulis, *Z. anorg. allgem. Chem.,* **230,** 65 (1936): See page 69 in particular.

(200) G. Spacu and G. Suciu, *Z. anal. Chem.,* **77,** 340 (1929).

(201) H. Bechhold and L. Gutlohn, *Z. angew. Chem.,* **37,** 494 (1924).

(202) G. Spacu and P. Spacu, *Z. anal. Chem.,* **93,** 260 (1933); G. Spacu and G. Suciu, *Z. anal. Chem.,* **79,** 196 (1930).

(203) Russ, *Z. anorg. allgem. Chem.,* **31,** 42 (1902).

(204) R. Ruer, *Z. anorg. allgem. Chem.* **42,** 87 (1913).

(205) P. N. Das-Gupta, *Journ. Indian Chem. Soc.,* **6,** 777; C. **1930,** I, 1305.

(206) A. Jílek and J. Kořa, *Z. anal. Chem.,* **87,** 422 (1931).

(207) A. Jílek and J. Kořa, *Z. anal. Chem.,* **89,** 345.

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